Advanced Functional Materials for Gas Sensing Applications: Trends and Challenges

Giorgio Sberveglieri

SENSOR Laboratory

CNR-INO & University of Brescia

http://sensor.ing.unibs.it/

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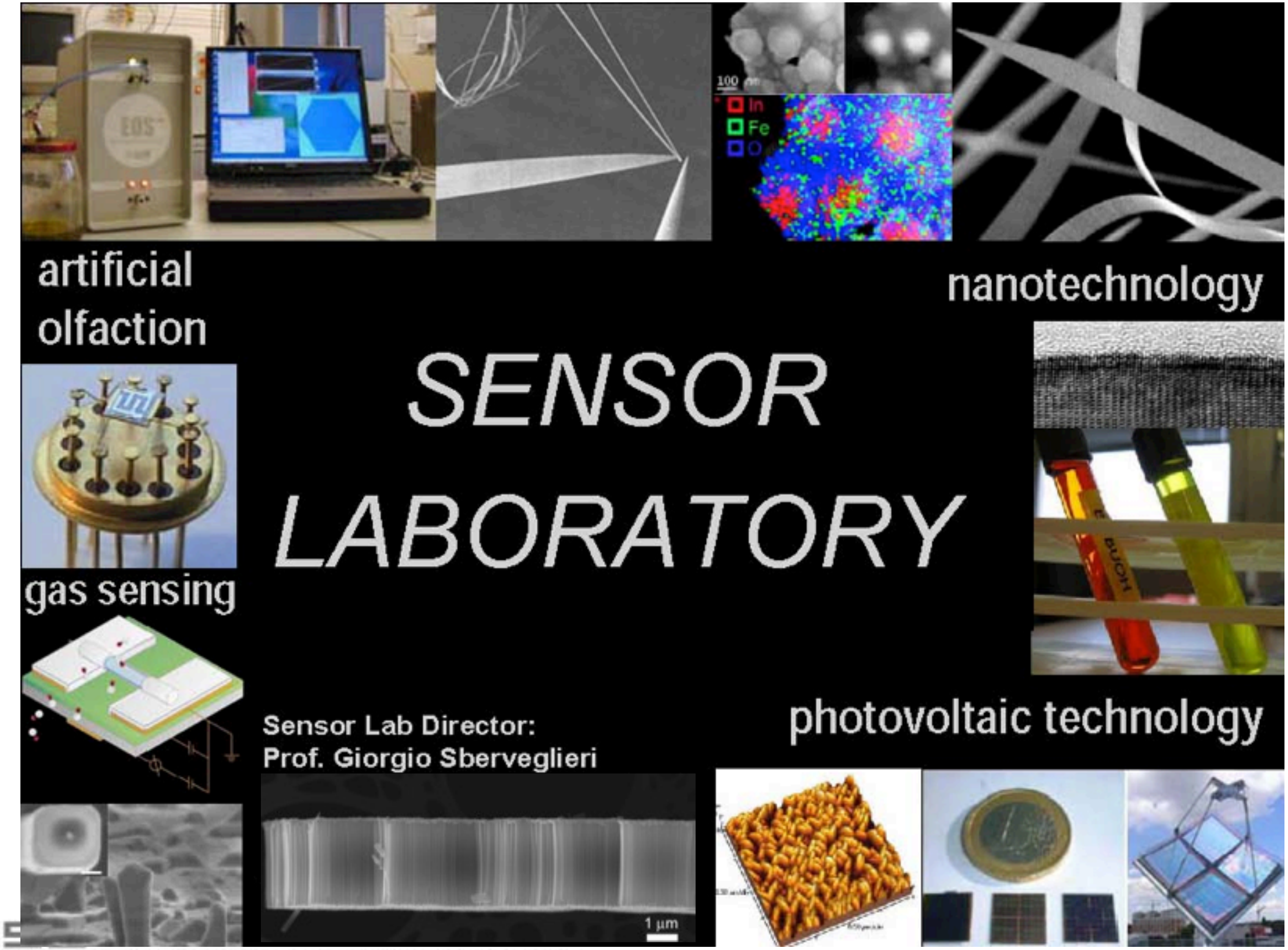
artificial olfaction
nanotechnology
SENSOR LABORATORY
gas sensing
Sensor Lab Director:
Prof. Giorgio Sberveglieri
photovoltaic technology
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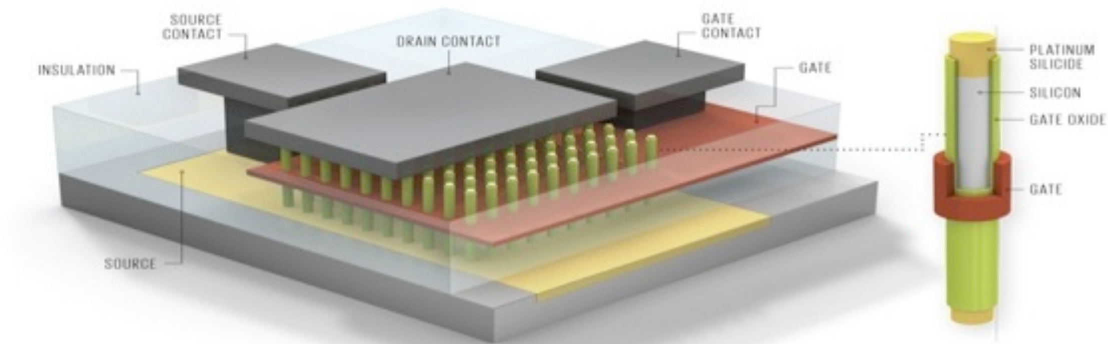
Outline

- Introduction
  - Devices miniaturization
  - Nanowires & gas sensors
- Preparation of metal oxide nanowire
- Chemical sensing devices
  - Stability, Sensitivity and Selectivity
  - Kelvin probe
  - (SI) Surface Ionisation
- Conclusions

Miniaturization

- Moore's Law for the advancement of integrated circuits followed since 1960s.
  - Nowadays researchers push nanolithography technology to its extreme limits to reduce the footprint of electronic devices,
- Nanowires have already brought fundamental changes to the future of the IC industry and will possibly allow keeping up with Moore's Law.
  - logic circuits, sensing and active elements for highly sensitive bio/chemical/photon sensors.
  - reliable and economic scaled-up processes that integrate nanowires into electronic devices.
    - This challenge needs to be urgently met if nanotechnology has to evolve beyond the academic interests.



Nanowire Transistors Could Keep Moore's Law Alive
By Alexander Hellemans
Illustration: Emily Cooper

Gas Sensors

- chemical or biological substances detection
- monitor industrial processes
- spoilage of food and toxic reagents during production
- Ubiquitous control of exposures to chemicals that may have negative effects on health

- Essential development scientific methods to assess, model and analyze exposure levels to potentially toxic compounds
- Measured gases are complex odor consisting in a mix of different analytes
  - Gas sensors arrays or electronic olfaction systems
- Chemiresistors simple architecture and easy signal processing

MOX chemical sensors

- Metal-oxides represent a category of materials with diversified properties covering all aspects of material science and physics in areas including superconductivity and magnetism
- Metal oxides are already established in the field of gas sensing
    - sensing mechanism: electrical resistance variation upon gas chemisorption
- In 1991 Yamazoe showed that reduction of crystallite size went along with a significant increase in sensor performance.

MOX gas sensors

- Technological challenge:
  - fabrication of materials with small crystallize size which maintained their stability over long term operation at high temperature
- A huge variety of devices have been developed mainly by an empirical approach and a lot of basic theoretical research and spectroscopy studies have been carried out to improve the well known “3S” of a gas sensor
  - Sensitivity, Selectivity and Stability

Why nanowires for chemical sensors

- Very large surface-to-volume ratio
- Downsizing of sensing materials improves the sensor performances
- Dimensions comparable to the extension of surface charge region
- Stability (high degree of crystalline order)
- Simple and low-cost preparation methods
- Possibility of selective chemical surface functionalization;
- Accommodate strain in presence of lattice mismatch
- Challenges: integration in macroscopic devices, good and stable electrical contacts

Preparation techniques

Two well-known and contrasting design strategies: top-down and bottom-up

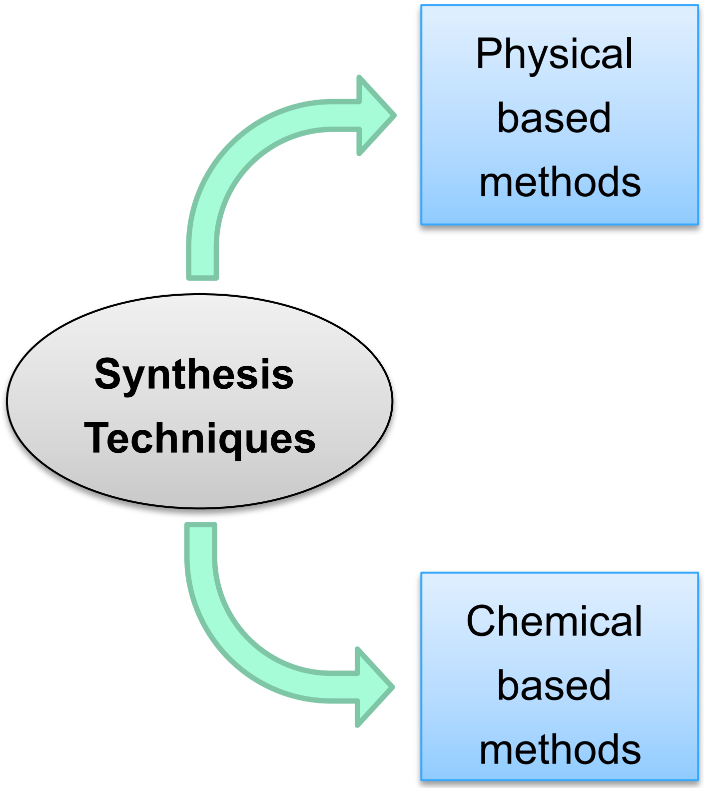
Top-down technologies are the staple of IC manufacturing and the semiconductor industry (lithography, thin-film deposition and etching)

Bottom-up strategies is a more natural approach and provide many attractive qualities

To capture the advantages of both methodologies:

- bottom-up synthesis of NWs with uniform size and consistent performance,
- assembly into highly ordered arrays that can interface with top-down fabrications

Synthesis Techniques



MOx nanostructures grow along a preferential direction, thanks to internal or external physical forces.

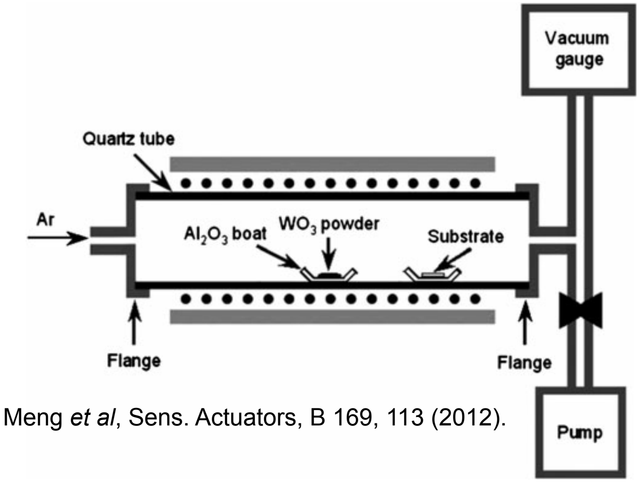
- Physical Vapour Deposition
- Electrospinning
- Pulsed Laser Deposition
- …

Chemical reactions are dominating the growth process.

- Chemical Vapour Deposition
- Thermal Oxidation
- Hydro & Solvothermal Growth
- Sol-Gel Synthesis
- …

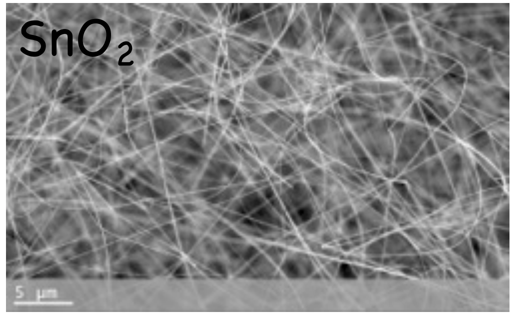
Physical and Chemical Vapour Deposition

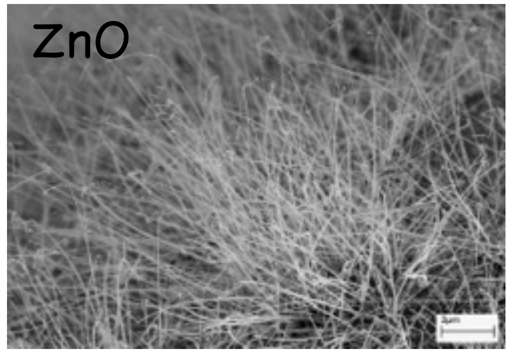
- In PVD, MOx powder is evaporated in a furnace at very high temperatures, in vacuum or at ambient pressure.
- Fabricated nanostructures:
  - SnO_2, ZnO, In_2O_3, WO_3 and $W_{18}O_{39}$
  - SnO2–ZnO heterojunctions
  - ZnO Surface-coated with organic modules

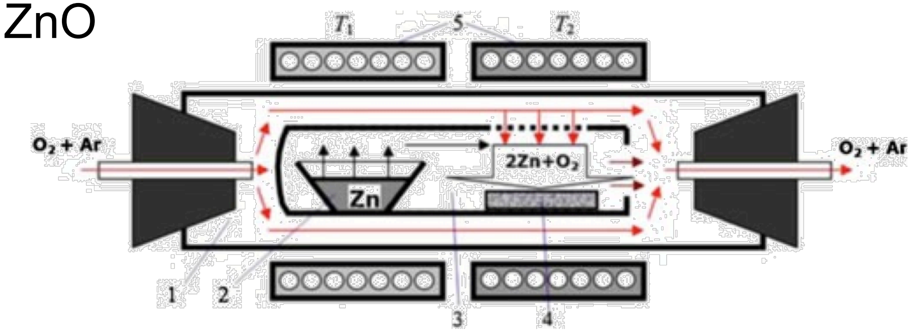


D. Meng *et al*, Sens. Actuators, B 169, 113 (2012).

- CVD technique consists in the reaction of volatile precursors flowing in the chamber for the production of MOx compounds on the substrates
- Fabricated nanostructures:
  - ZnO, In_2O_3, TiO_2 and SnO_2
  - Cr_2O_3–ZnO core–shell heterojunction
  - Metal-doped ZnO



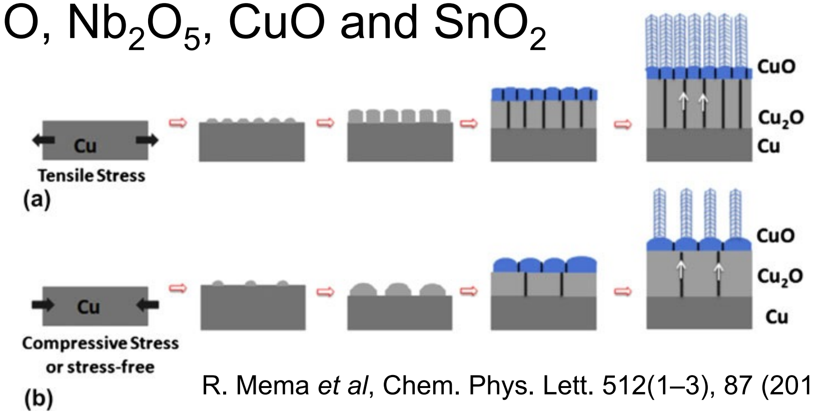




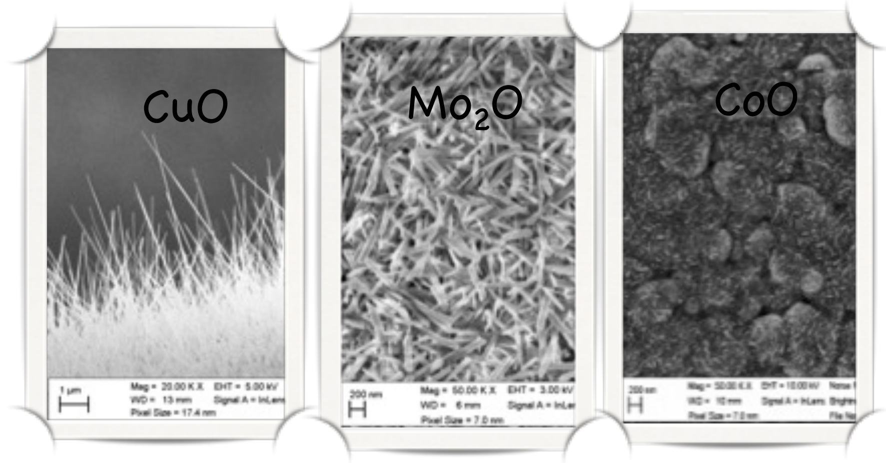
O. Lupan *et al*, Mater. Res. Bull. 45(8), 1026 (2010).

Thermal Oxidation and Electrospinning

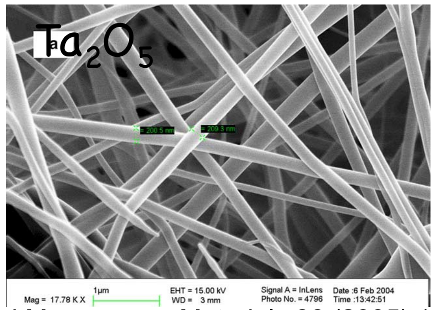
- Thermally assisted oxidation of a metal layer or stub in an oxidizing atmosphere.
- Fabricated nanostructures:
  - ZnO, Nb_2O_5, CuO and SnO_2



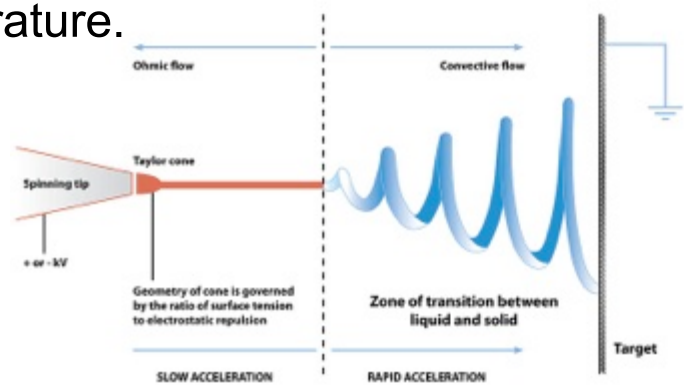
R. Mema *et al*, Chem. Phys. Lett. 512(1–3), 87 (2011).



- Electrospinning technique uses an electrical charge to fabricate very fine wires from a liquid.
- High temperature is not required to produce the nanostructures and thus is a very attractive synthesis method at low fabricating temperature.
- Fabricated nanostructures:
  - ZnO, TiO_2 and SnO_2



Minedys Macìas et al, Microporous and Mesoporous Materials 86 (2005) 1–13



Source: wikipedia

Integration into functional devices

- Integration strategy is strongly related to synthesis process.

Mox Synthesis → Integration → Functional Device

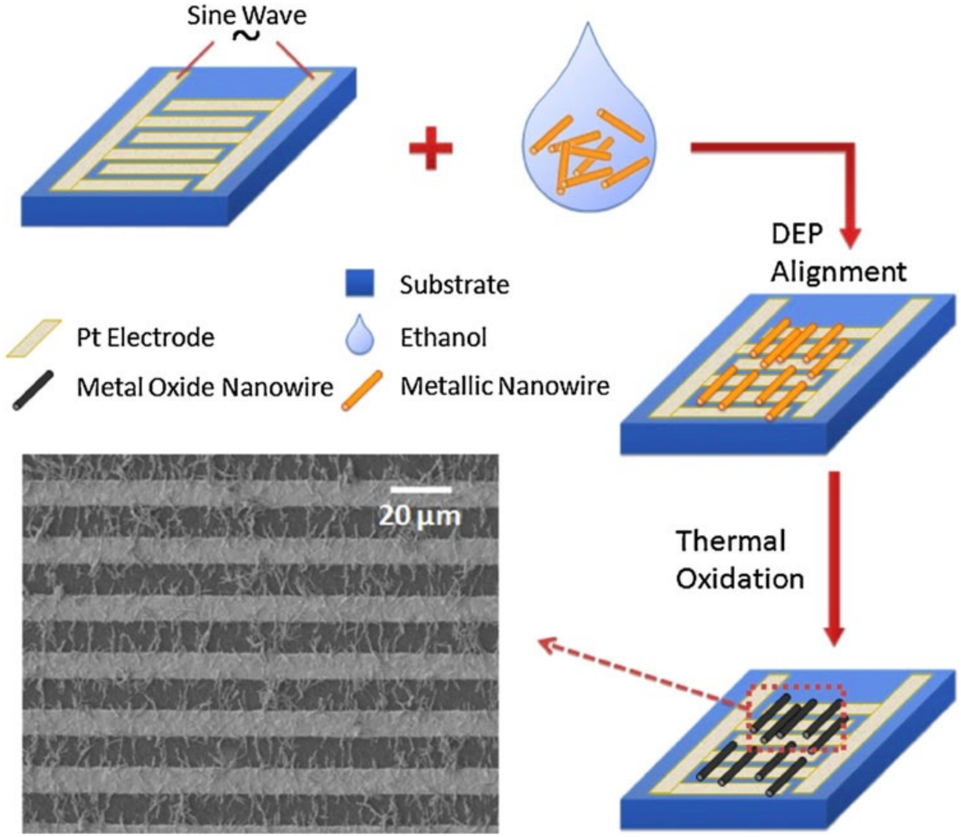
Mat Based Devices | **Single NW Devices**

- Conventional techniques:
  - Metal deposition
  - Silver gluing
  - …

- Alignment is critical.
- Expensive techniques:
  - Focused Ion Beam
  - Electron Beam Litography
  - …

Mat-based Devices

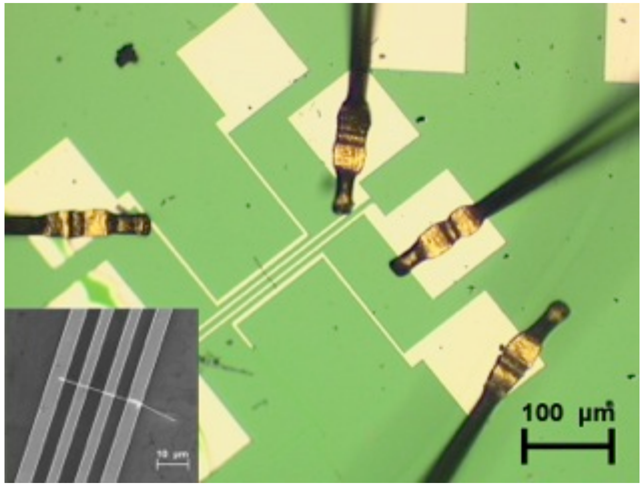
- Electrodes are required to fabricate functional mat-based devices.
- Different tecniques could be use:
  - ✓ Thermal metal evaporation
  - ✓ Shadow-masking sputtering
  - ✓ Silver glue
  - ✓ Lithography (Optical or Electronic)
  - ✓ Electrophoresis

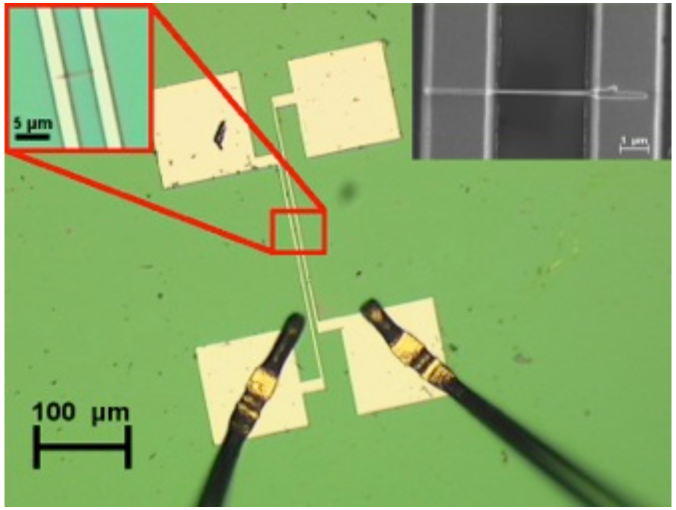


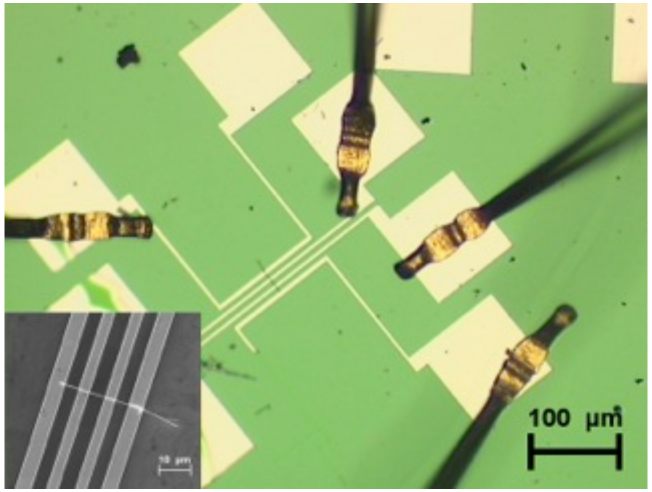
Schematic diagram of sensor chip fabricating procedure using dielectrophoresis and top view of the sensor chip surface. X.P. Li *et al*, Sens. Actuators, B 158(1), 199 (2011).

Single NWs Devices

- Single NW Devices are much more complex and expansive to fabricate.
- Alignment is very crucial, because it could be difficult to locate a single nanowire on the substrate.
- Some tecniques could be use:
  - ✓ Electron Beam Lithography
  - ✓ Electrophoresis
  - ✓ Focused Ion Beam







MOX NWs Gas Sensors

- **Conductometric gas sensors**
- Comini E, Faglia G, Sberveglieri G, Pan ZW, Wang ZL. (2002) Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts. Appl. Phys. Lett. 81, 1869–71

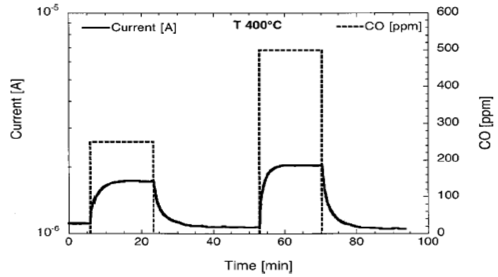


FIG. 2. Response of the SnO_2 nanobelts to CO at a working temperature of 400 °C and 30% RH.

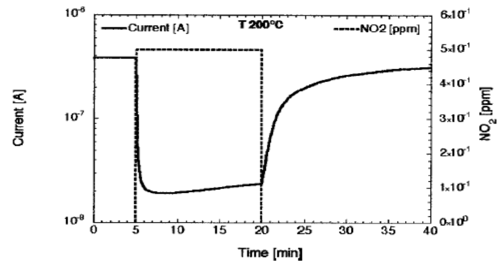
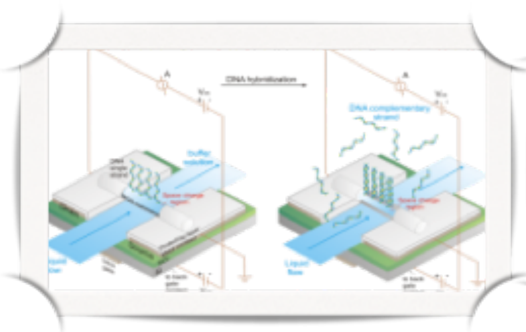
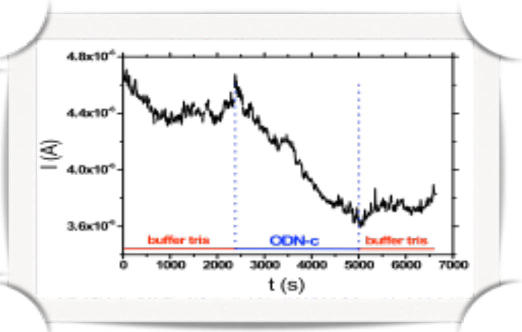


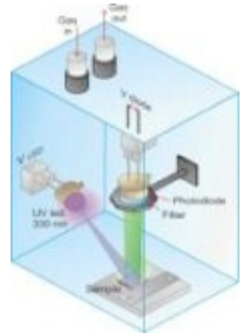
FIG. 4. Response of the SnO_2 nanobelts to NO_2 at a working temperature of 200 °C and 30% RH.

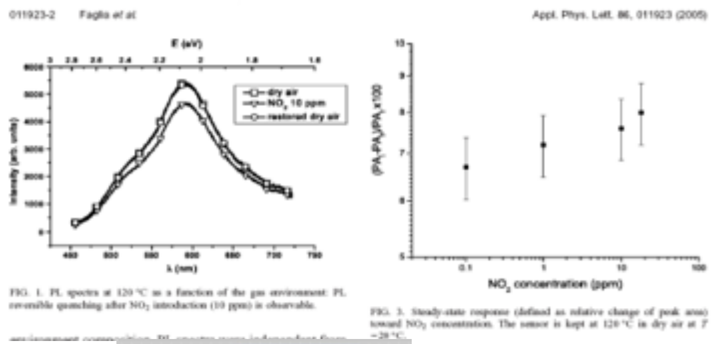
- **Single Nanowire Transistor for biochemical sensing**



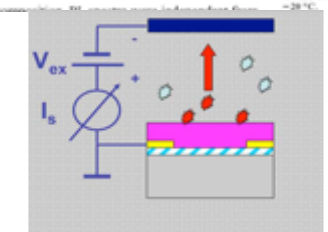


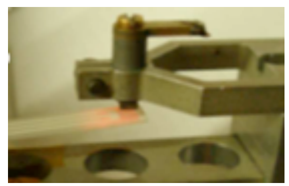
- **Optical gas sensors**
- Faglia G, Baratto C, Sberveglieri G, Zha M. and Zappettini A. 2005. Adsorption effects of NO2 at ppm level on visible photoluminescence response of SnO2 nanobelts, Appl. Phys.Lett. 86



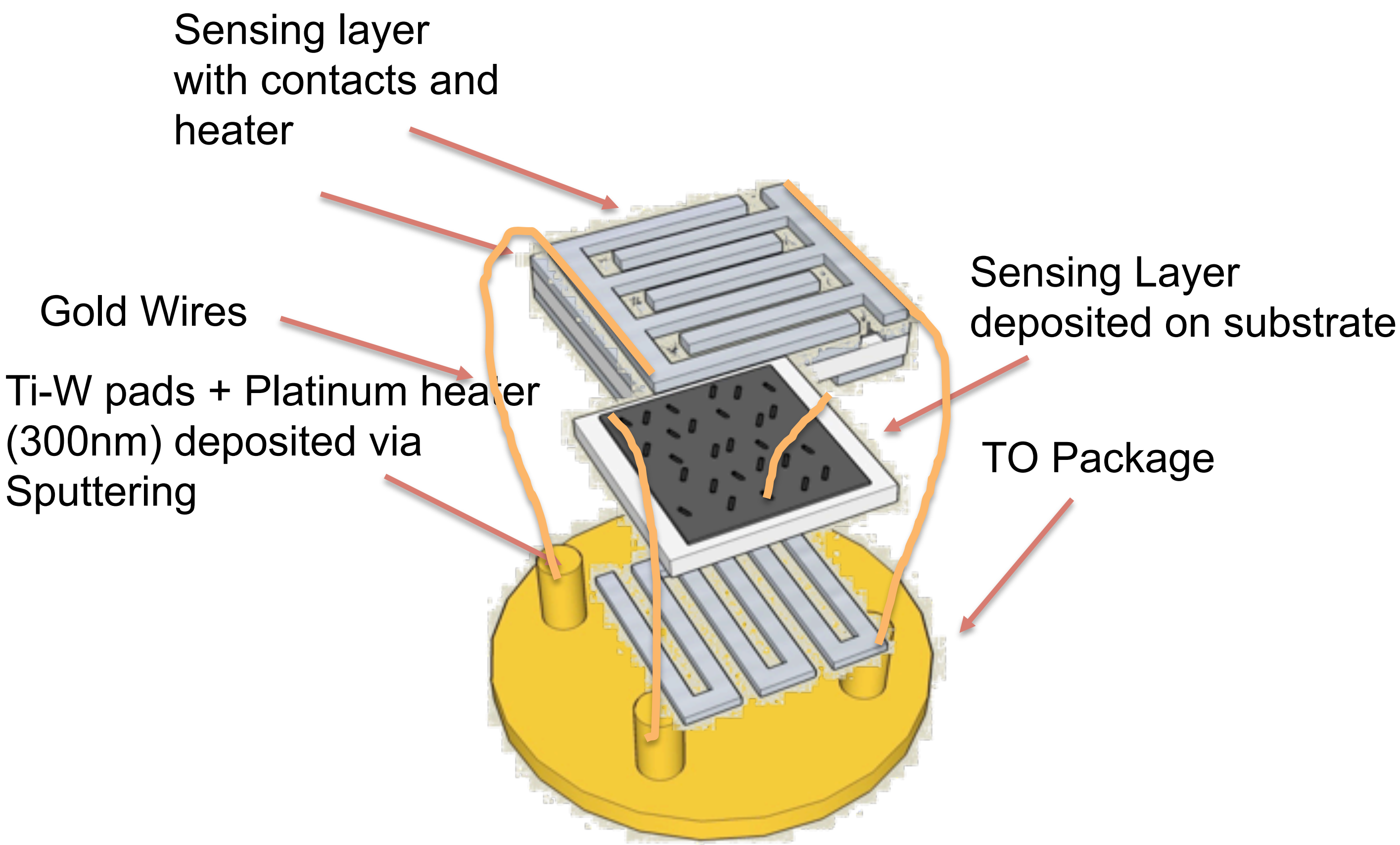


- **Surface ionization chemical sensors**
- A. Hackner, A. Habauzit, G. Müller, E. Comini, G. Faglia, and G. Sberveglieri; IEEE Sens. J. 9 (2009) 1727





NWs Chemical Sensors



NWs Chemical Sensors

- Flexible chemical sensors
- (SI) Surface Ionisation sensors
- Kelvin probe

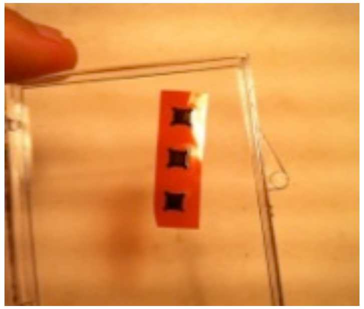
- Stability, Sensitivity and Selectivity ?

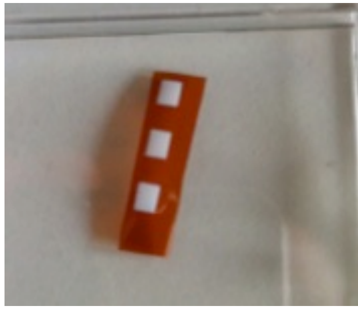
Flexible Chemical Sensors

Flexible Substrates

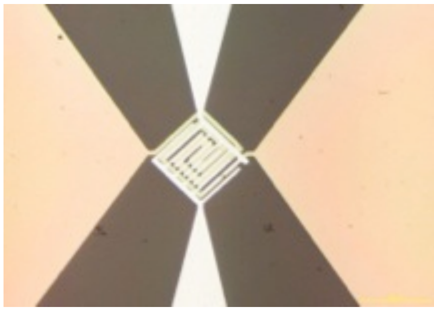
- Thermal oxidation technique is compatible with flexible transducers:

Kapton



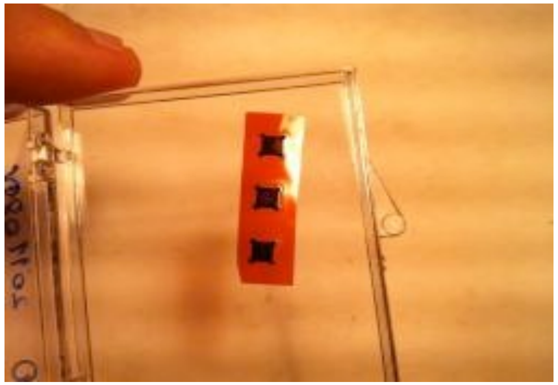


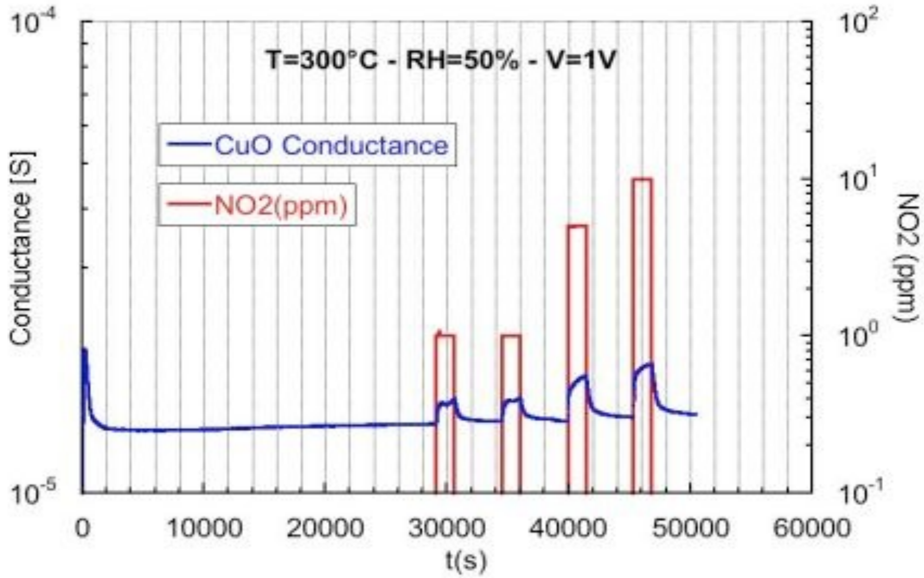
Polyimide



Flexible Substrates (Kapton - CuO)

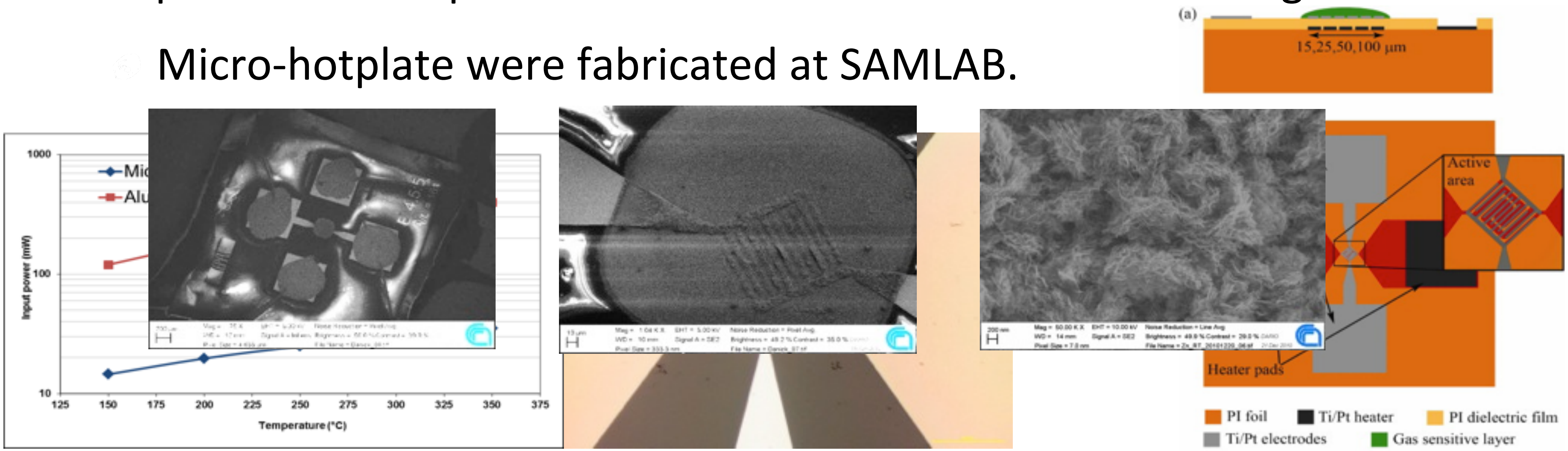
- Commercial Kapton was used as flexible plastic substrate.
- Cu films were deposited via sputtering (1.8µm, 50WRF Argon plasma, 4.3x10-3 Torr, RT)
- Oxidation temperature 300°C in a 80% O2 – 20% Ar atmosphere.





ZnO on Polyimide micro-hotplates (EPFL)

- Micro-hotplates are the key elements to reduce the power consumption of metal-oxide chemical sensors.
- Thanks to the micro-size dimensions it is possible to achieve a power consumption reduction of almost one order of magnitude.
- Micro-hotplate were fabricated at SAMLAB.

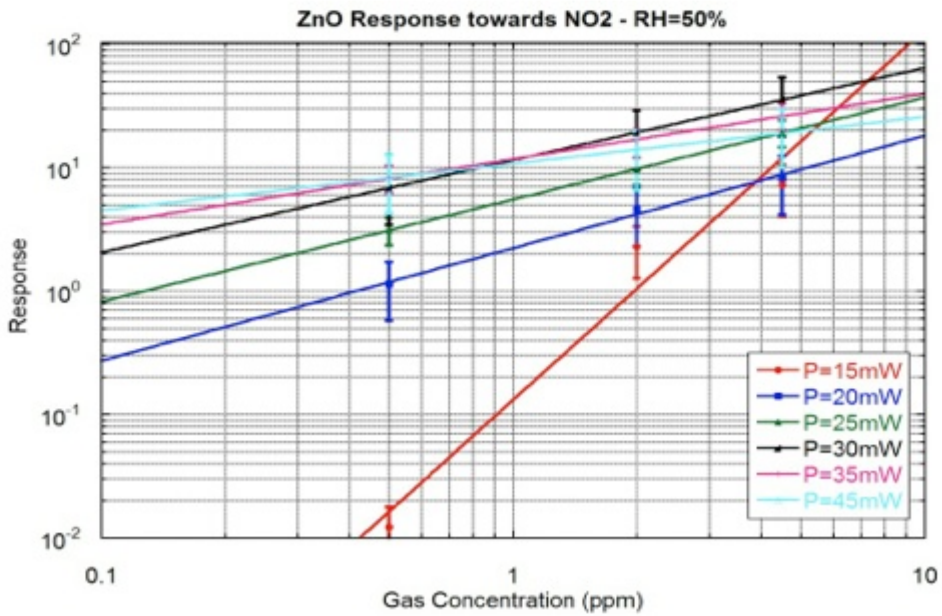


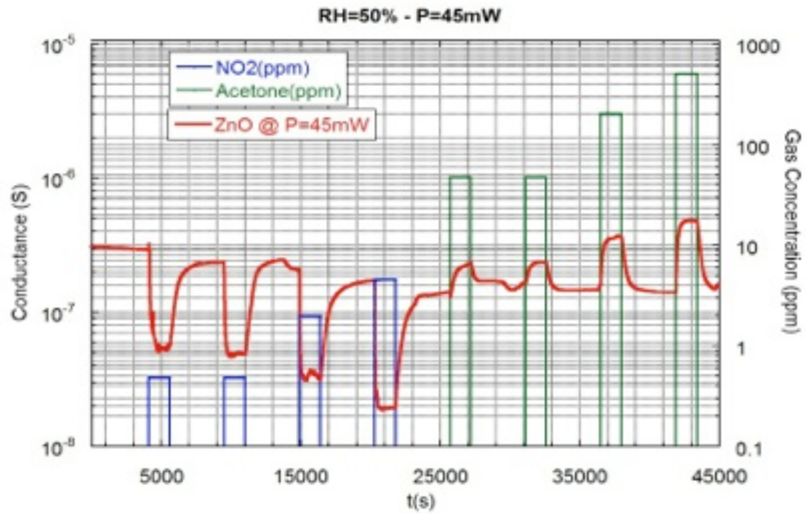
Functional Characterization (ZnO)

- Calibration curves for NO2 with 15-45mW
- Relative humidity fix at 50%
- Oxidizing Gas: $Response = \frac{G_{Gas} - G_{Air}}{G_{Air}}$
- Reducing Gas: $Response = \frac{G_{Air} - G_{Gas}}{G_{Gas}}$

$$Response = A * [gas\ concentration]^B$$

- Good performance towards NO_2 (>7@500ppb), in line with other works reported in literature#.





#M.-W. Ahn et al. / Sensors and Actuators B 138 (200

Tonny-Roksana Rashid , Duy-Thach Phan , Gwiy-Sang Chung

Sensors and Actuators B: Chemical, Volume 185, 2013, 777 - 784

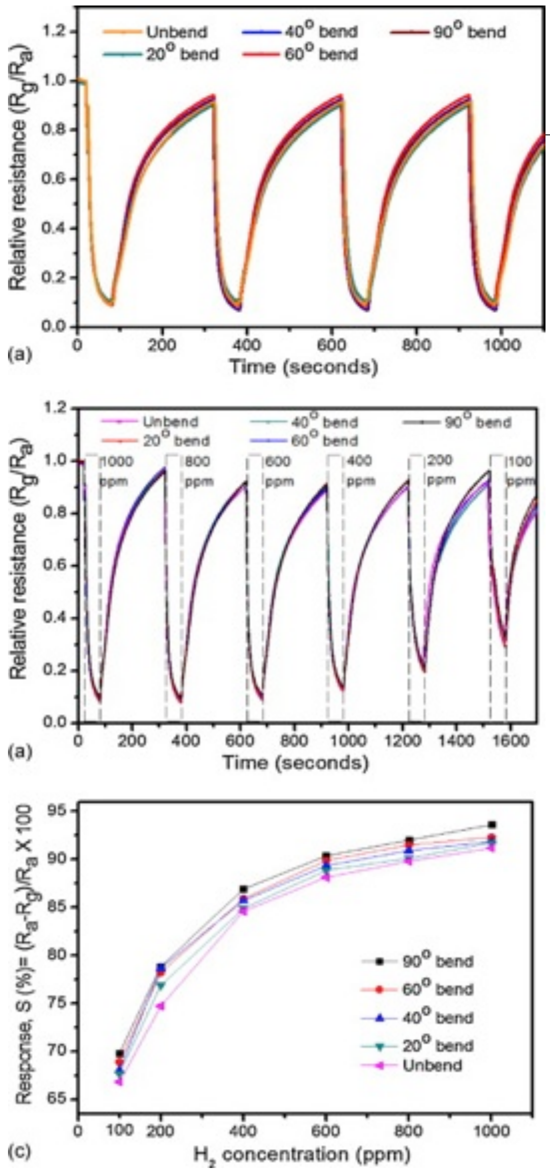


Fig. 8 Performance of the flexible sensor for variou: bending angles (0°, 20°, 40°, 60°, 90°) for 15 s Pd l((a) repeatability at 1000 ppm, and (b) and (c) sensor response at various concentrations.

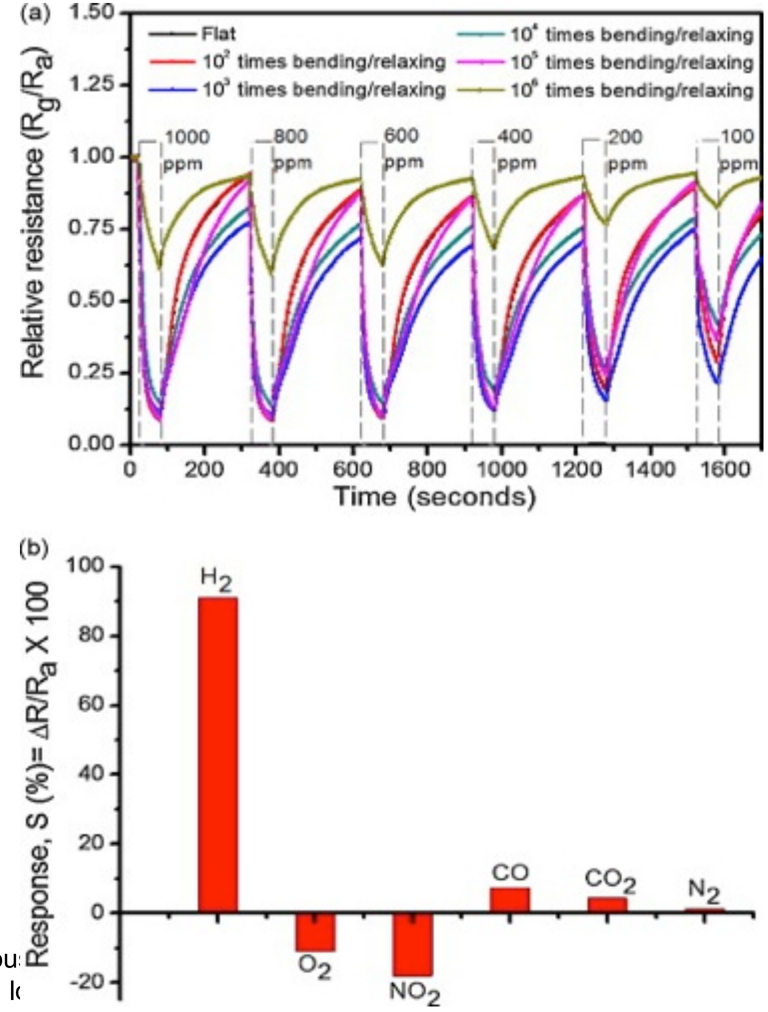
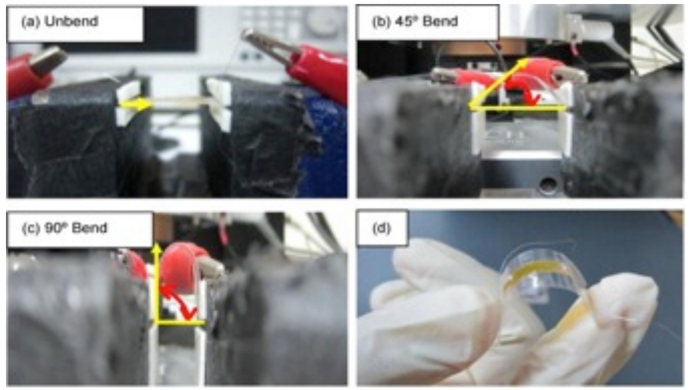
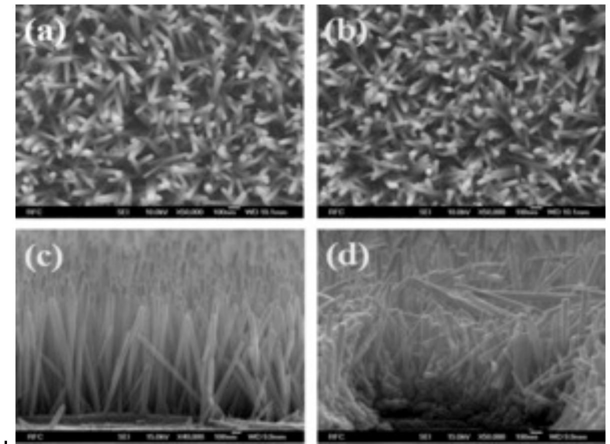


Fig. 9 (a) The reliability test of the flexible sensor and (b) selectivity of sensors with various gases (15 s Pd sample).

Fig. 6 Optical images: (a) un-bending (curvature angle of 0°), bending at curvature angle (b) ~45°, (c) ~90°, and (d) flexible H 2 sensor.





Flexible Paper Sensors

- low cost, ubiquitous available in different forms
- high surface area (microfiber composition)
- amenable to printing technologies
- strong adhesion to a variety of materials
- it may be cut using low cost tools and standard techniques
- great global impact -> offer a completely new approach to environmental and health care monitoring

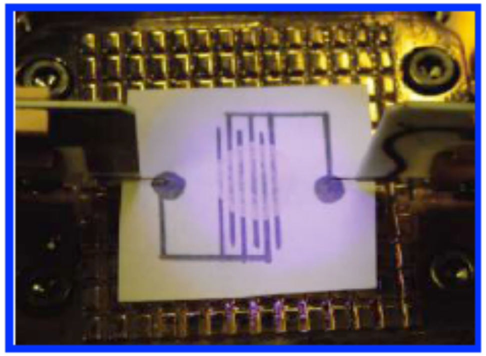


Figure 1. Interdigitized sensor on a paper substrate conn probe station *J. Phys. Chem. C, Vol. 115, No. 1, 2011*

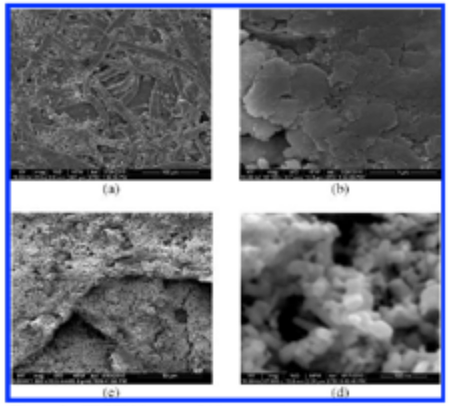
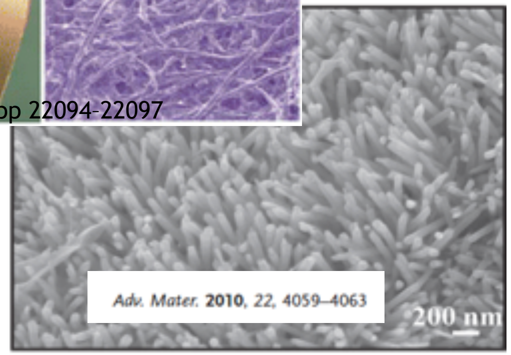
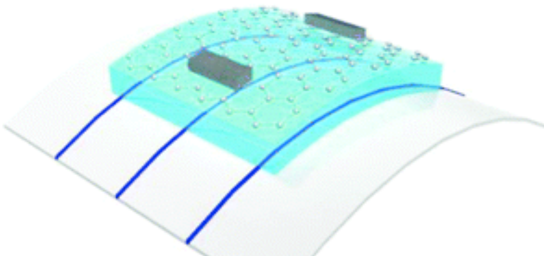


Figure 2. FE-SEM images of (a) paper substrate, (b) graphite lines, (c) ZnO crystals on paper, and (d) ZnO crystals on paper.

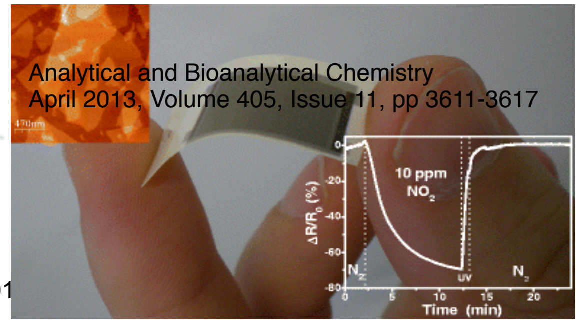
J. Phys. Chem. C, **2012**, *116* (41), pp 22094-22097



Adv. Mater. **2010**, 22, 4059–4063



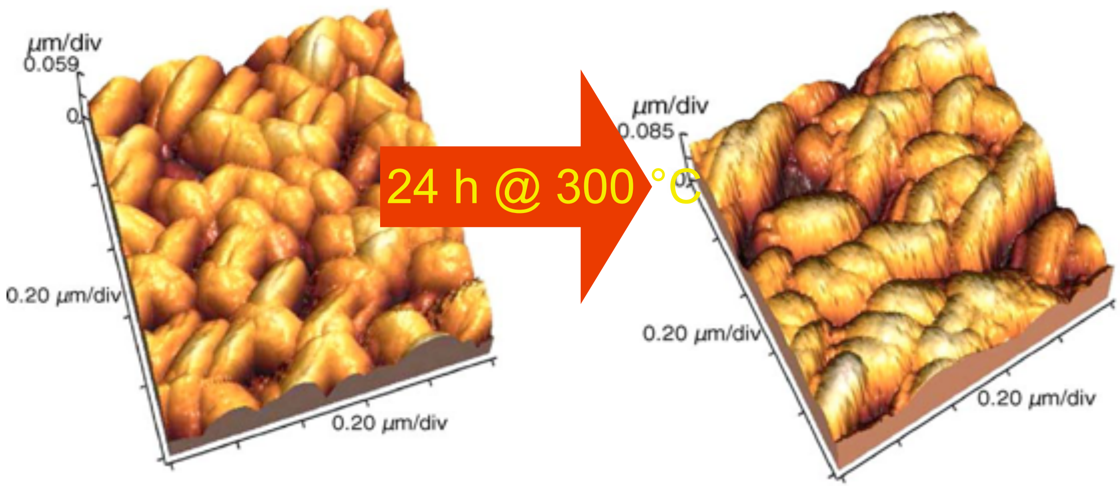
Phys. Chem. Chem. Phys., 2013,**15**, 1798-1801

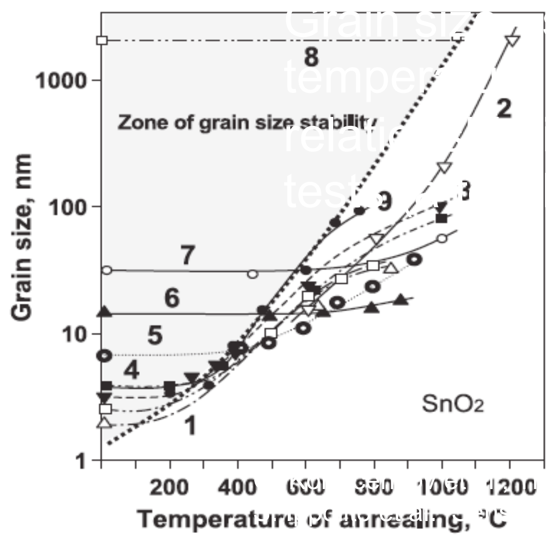


Analytical and Bioanalytical Chemistry
April 2013, Volume 405, Issue 11, pp 3611-3617

Stability

Stability - thermal effects





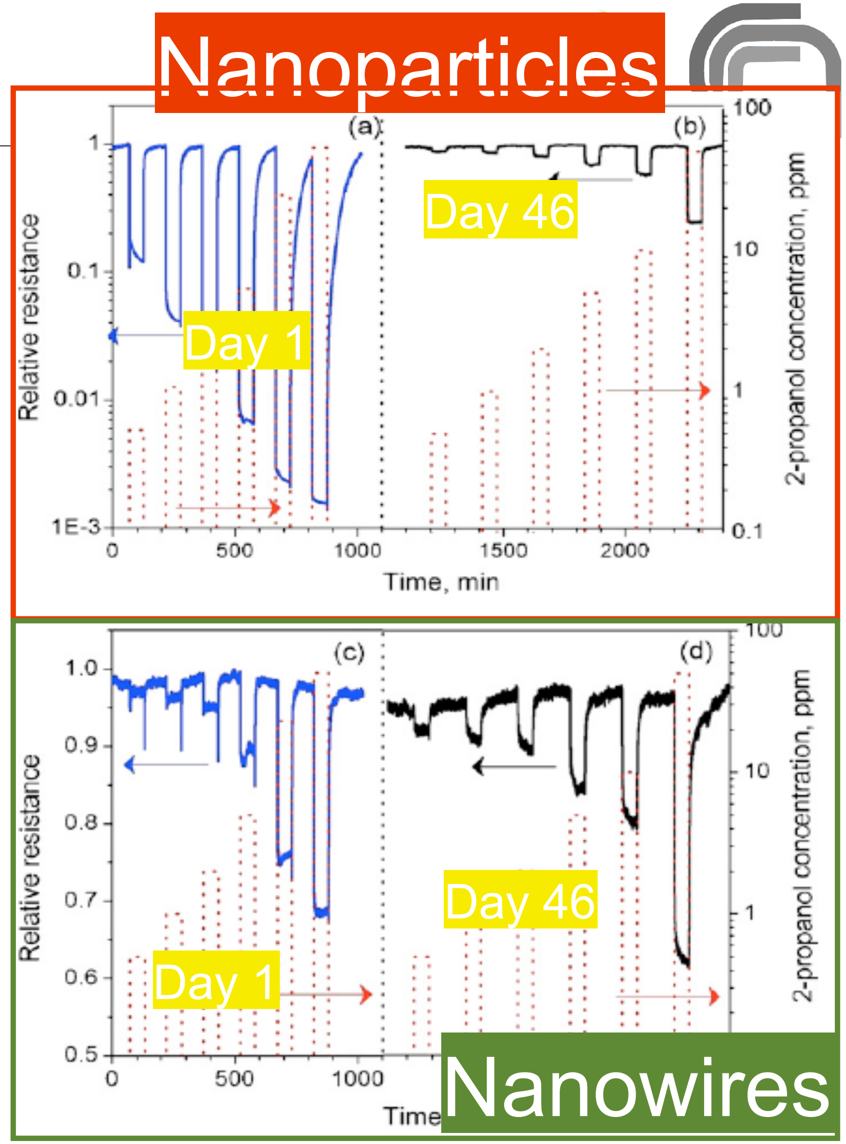


Fig. 2. The change of the SnO_2 nanostructures resistance of median sensor segment relative to the maximum value under the exposure to 2-propanol vapors of step changed concentration at 1st day (a and c) and 46th day (b and d): (a and b)—NP 3-D layer; (c and d)—NW 2-D mat.

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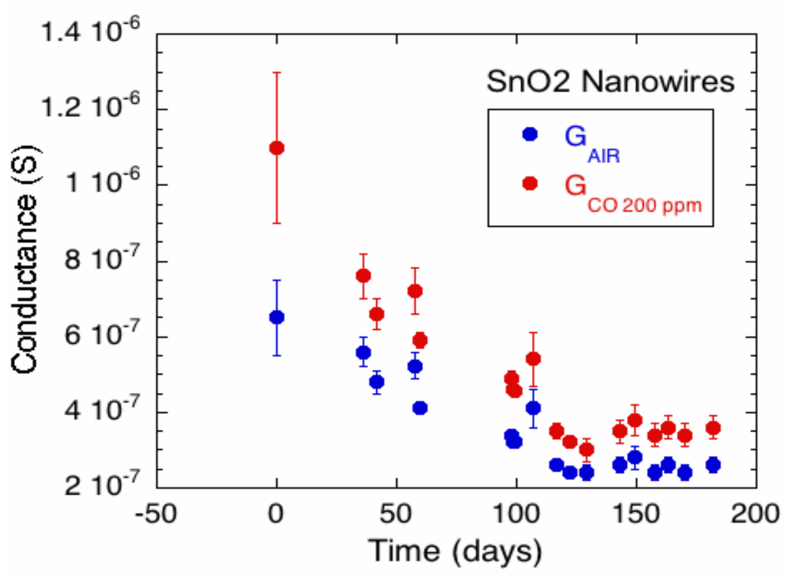
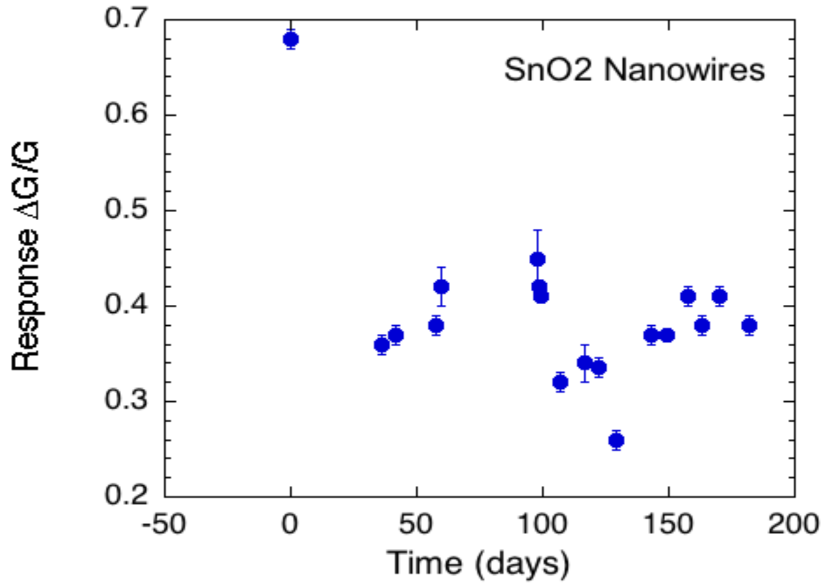
Stability - thermal effects



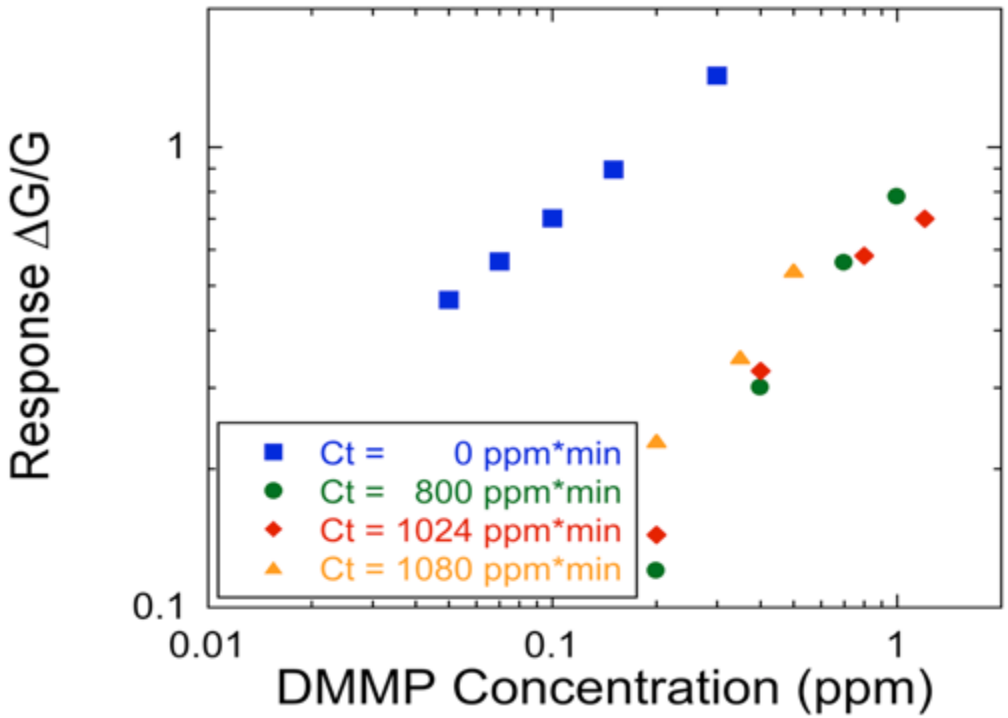


We used CO to test the thermal stability of gas sensors because CO exhibit almost no poisoning effects;

Both the baseline and the conductance value during gas exposure (CO 200 ppm) exhibit a similar drift toward lower values during the first 100 days, then both reach a steady state;

No drift is observed for sensor response $\Delta G/G$, which is better described by means of a mean value and its std: $\Delta G/G = 0.38 \pm 0.05$.

Stability - DMMP poisoning effects



- **Background from catalysis field:**
  - DMMP dissociates over the oxide surface leaving phosphorous compounds that poison the catalyst layer decreasing its capability to further decompose DMMP
  - Poisoning effects observed working with 1000 ppm for 10 hours, corresponding concentration per time values Ct ≈ 10^6 ppm*min

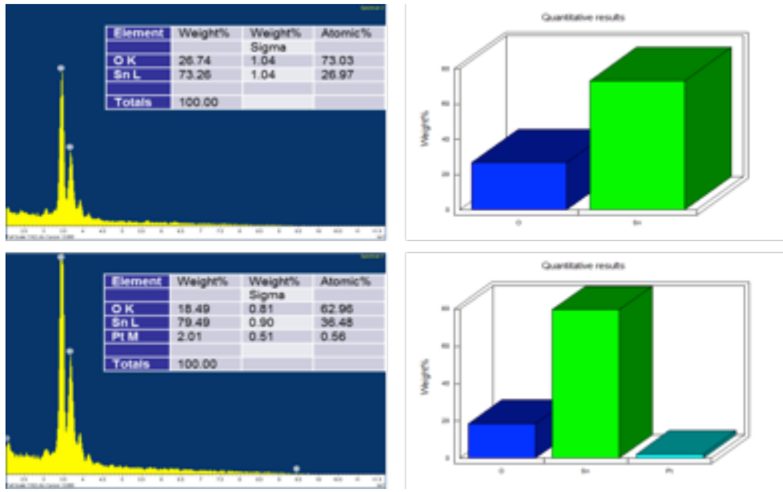
❖ **Gas sensor field**
  - the initial capability to respond to 30 ppb of DMMP decreases with exposure to DMMP till reaching a steady state regime
  - to develop (and train) an electronic nose it's necessary to repeat DMMP exposures - sensors working in the 2nd regime, despite less responsive,are preferred because of their enhanced stability
  - Poisoning effects can be observed at Ct values of the order of 100 ppm*min
  - After an exposure of about 1000 ppm*min sensors reach a nearly stable regime

Sensitivity/ Selectivity

Surface functionalisation

- Metal particles were deposited by magnetron sputtering on top of SnO_2 NWs, in different atomic weight ratios: 0%, 1% and 3%.

- EDX performed on samples:
    - Pt 1% --> 1.2%
    - Pt 3% --> 2.6%

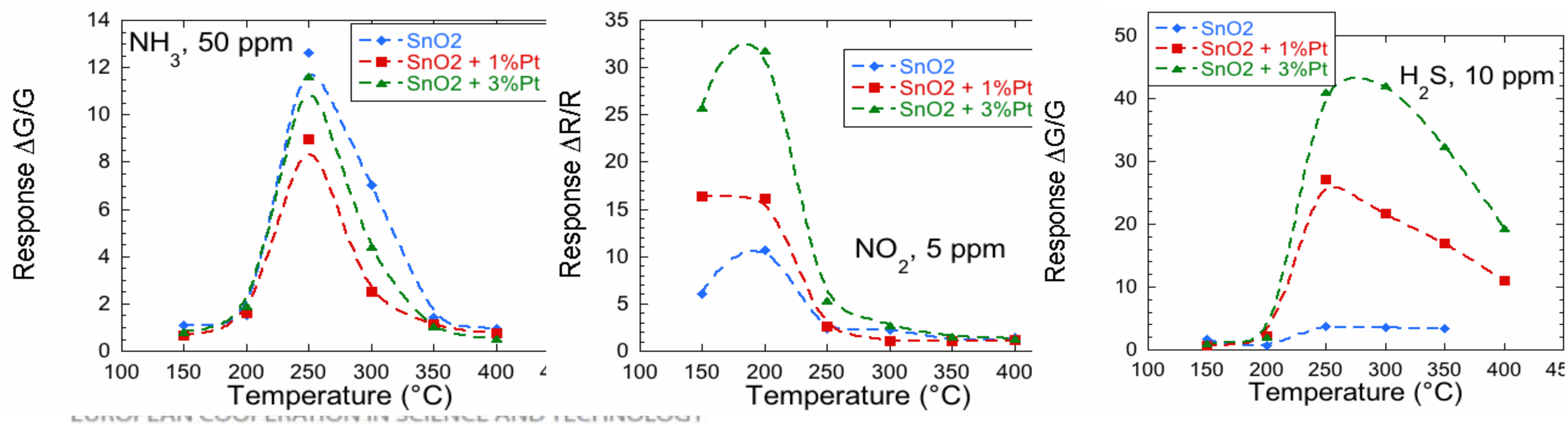


Pt 0%

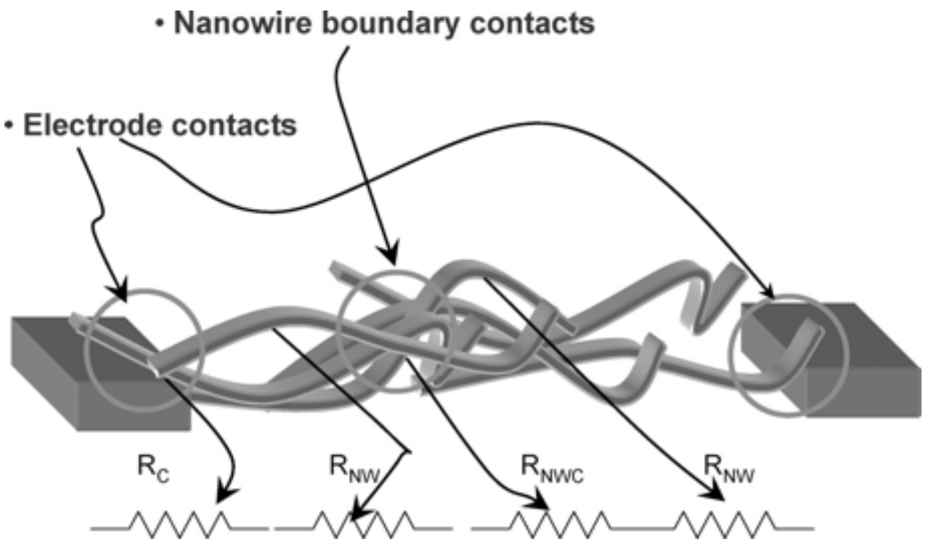
Pt 3%

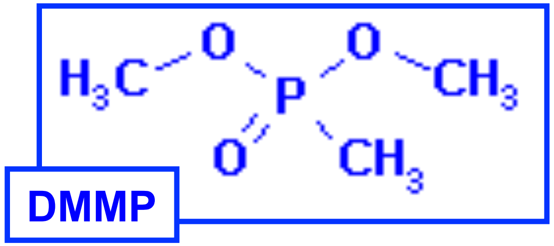
Electrical Measurements

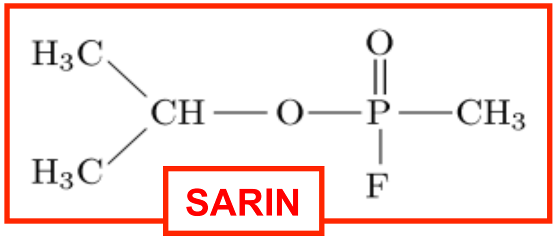
- Response to NH_3
  - Optimal temperature (250°C) is not influenced by the metal functionalization
  - Influence of metal is almost negligible
- Response to NO_2 and H_2S
  - Increasing the Pt ratio on SnO_2 NWs samples has a positive effect

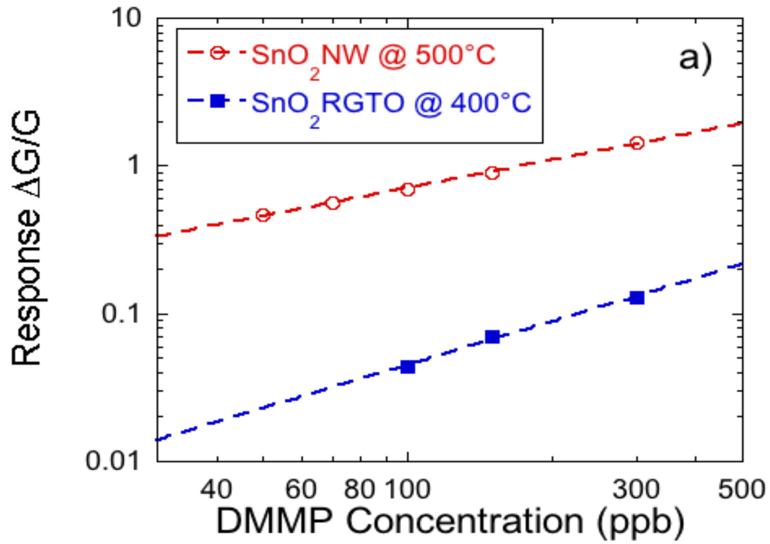


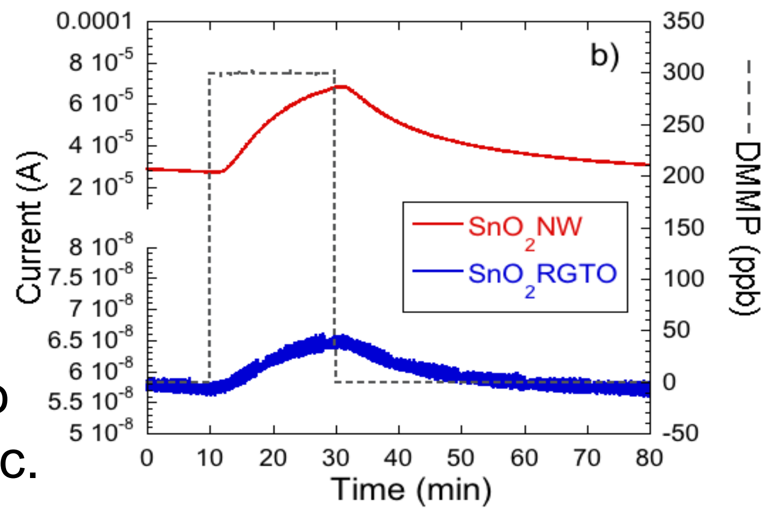
Chemiresitors – Sensitivity







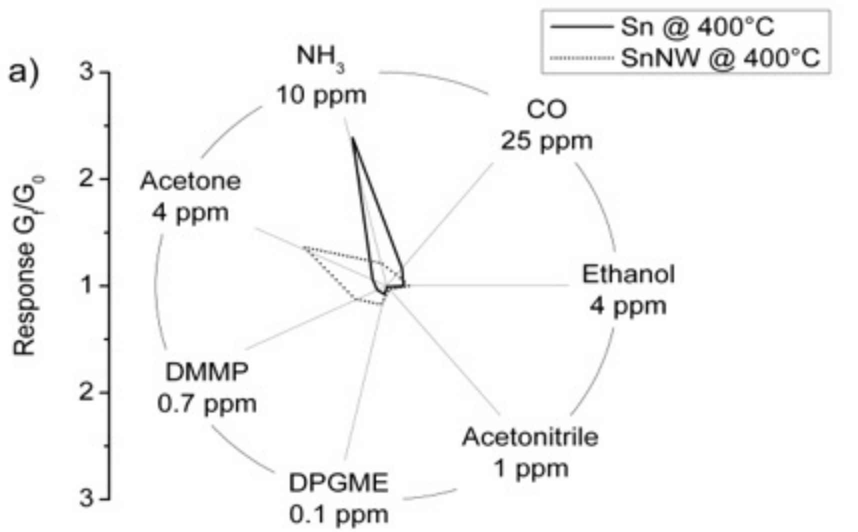


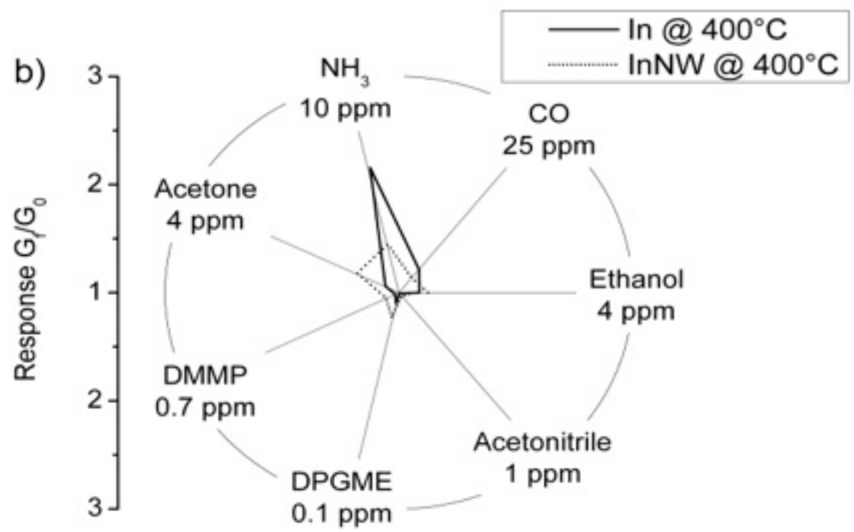


- DMMP simulant for Sarin nerve agent
- Sarin threshold limit: 30 ppb
- Nanowire based chemiresistors are able to respond to DMMP concentrations close to the Sarin threshold conc.

A. Fort et al., Sens. Actuators B 148, 283 (2010)

Chemiresitors - Selectivity



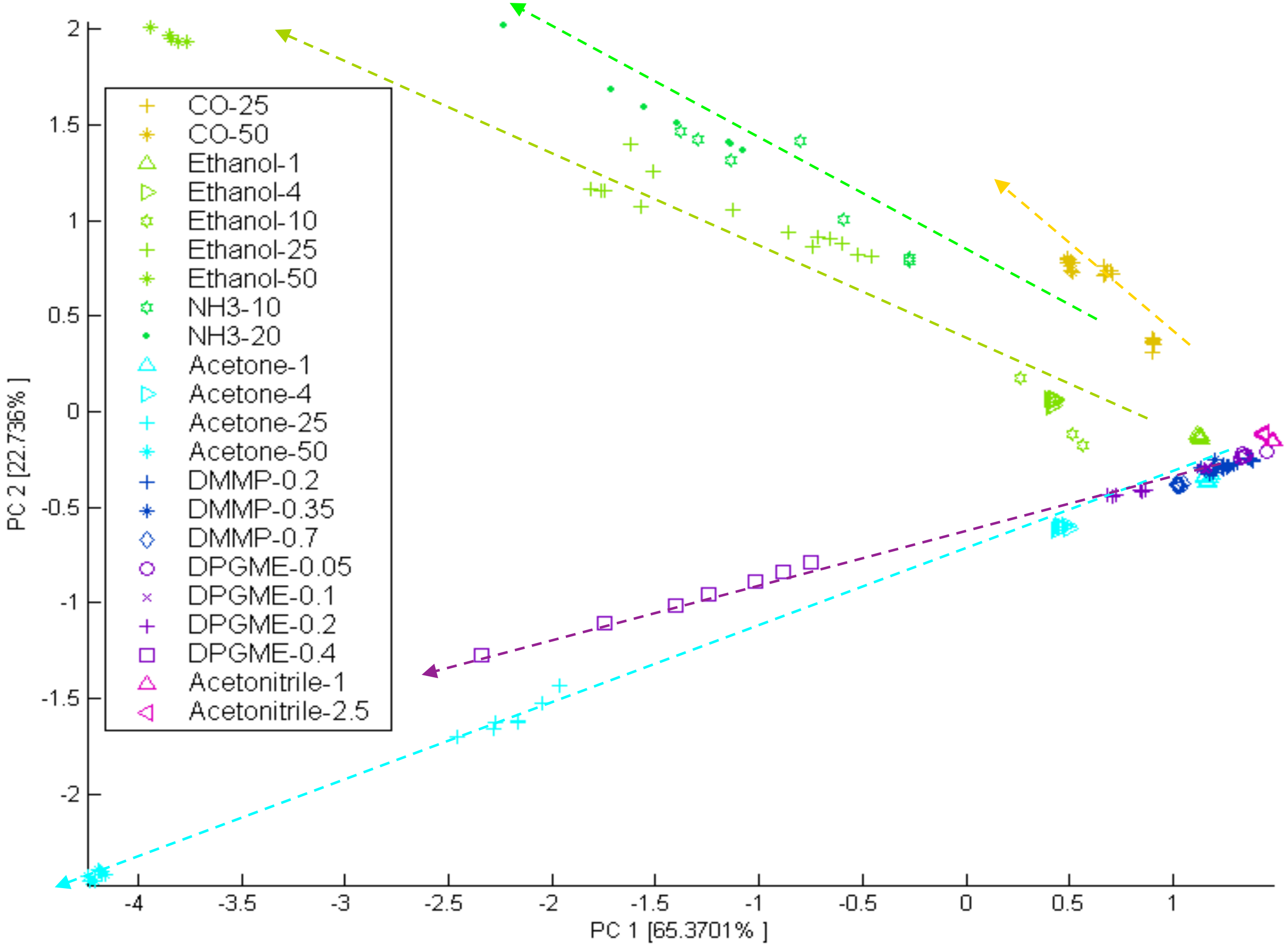


•Nanowires are not more sensitive than their thin-films counterparts in general, but sensitivity is related to the target gas.
•These differences are useful to develop an electronic nose suitable to distinguish different chemicals (avoid/reduce false alarms).

A. Ponzoni et al., IEEE Sensors J. 8 (2008), 735-742.

Chemiresitors – Selectivity

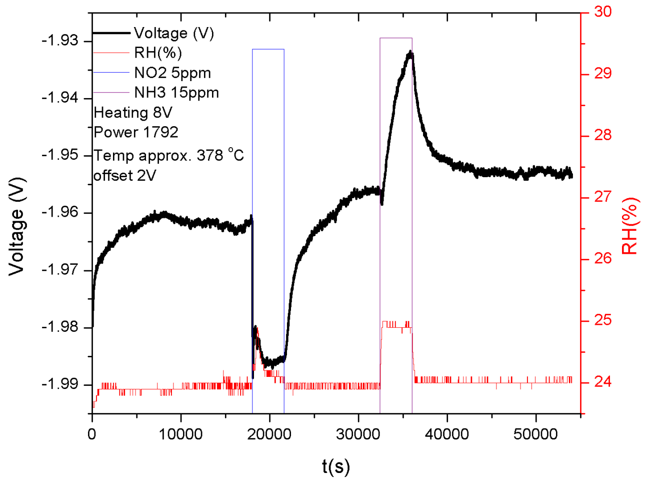
Mixed array: thin films (SnIn, SnAu) + nanowires (Sn, In) toward an integrated electronic nose (nanowires+ thin films)

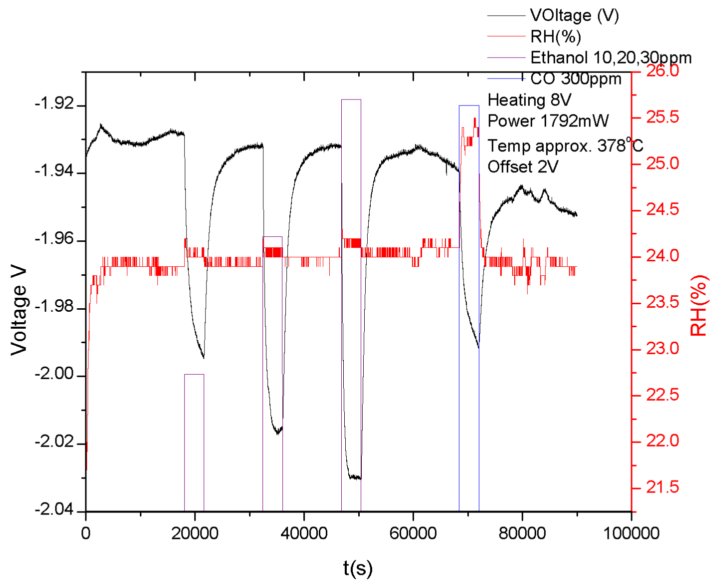


Work Function Investigation of p-type oxides for sensing: *CuO nanowires*

❖ Conductivity reading of p type materials for gas sensing is quite unsatisfying because surface reactions affects the density of majority carriers

❖ Work Function based detection is instead feasible for reducing gases as EtOH





Surface Ionization (SI) phenomena

positive ions

$$\alpha = \frac{n_+}{n_0} = A_+ \exp\frac{q(\varphi - V_+)}{kT}$$

negative ions

$$\alpha = \frac{n_-}{n_0} = A_- \exp\frac{q(V_- - \varphi)}{kT}$$

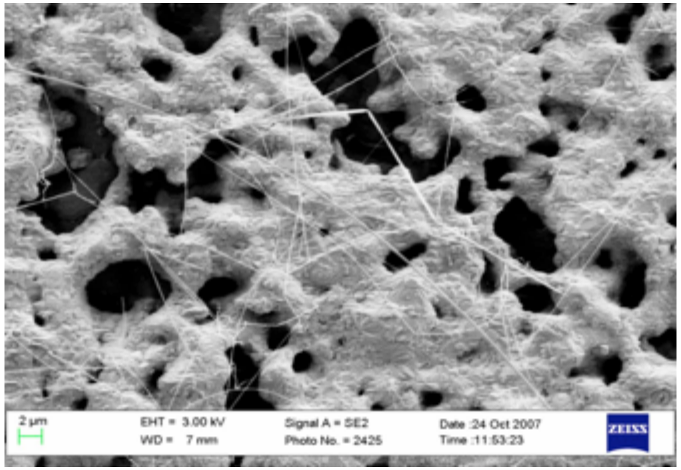
Degree of surface ionization α (ratio between the concentration of ionized and neutral ions) depends on the layer work function φ and on the molecule ionization potential (V_+) or electron affinity (V_-)

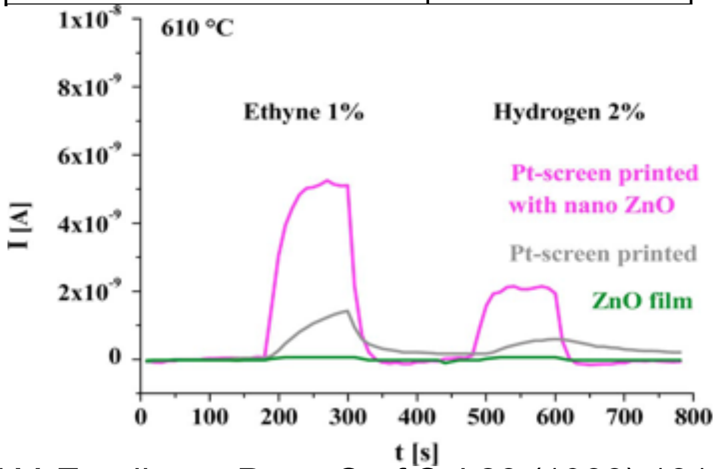
→ **Selectivity**

Molecule	**qV_+ (eV)**
Acetone	9.703
Ethanol	10.48
O_2	12.07
CO	14.01
NO_2	9.586

NANOWIRES

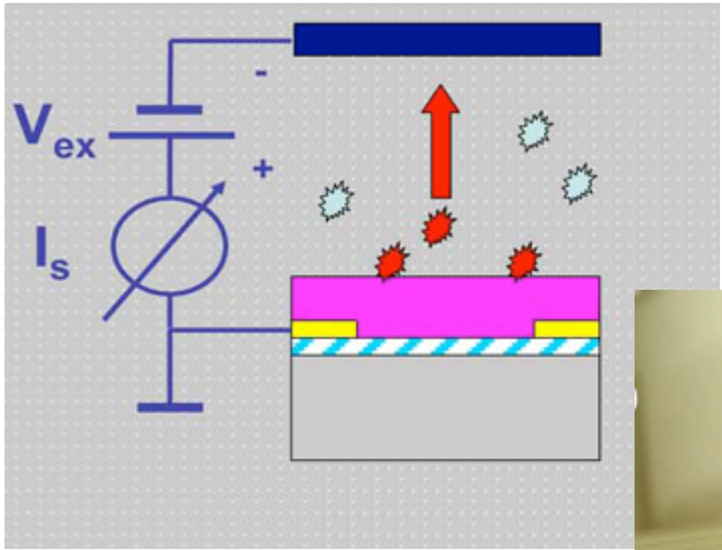
CAPABILITY OF HIGH ASPECT RATIO NANOSTRUCTURES TO CONCENTRATE HIGH ELECTRIC FIELDS AT THEIR APEX





U.K Rasulev , E.Y. Zandberg; Progr.Surf.Sci.28 (1988) 181

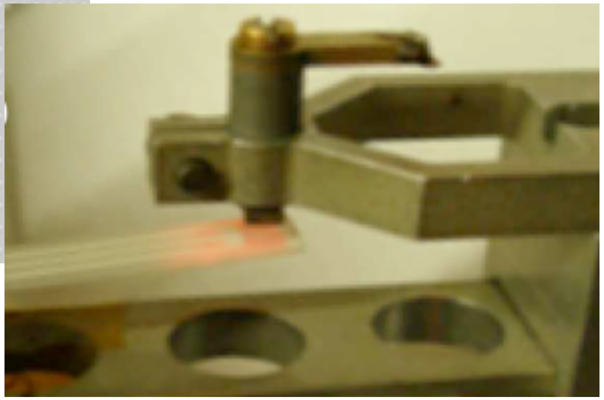
Surface ionization (SI) - vertical layout



Typical experimental parameters

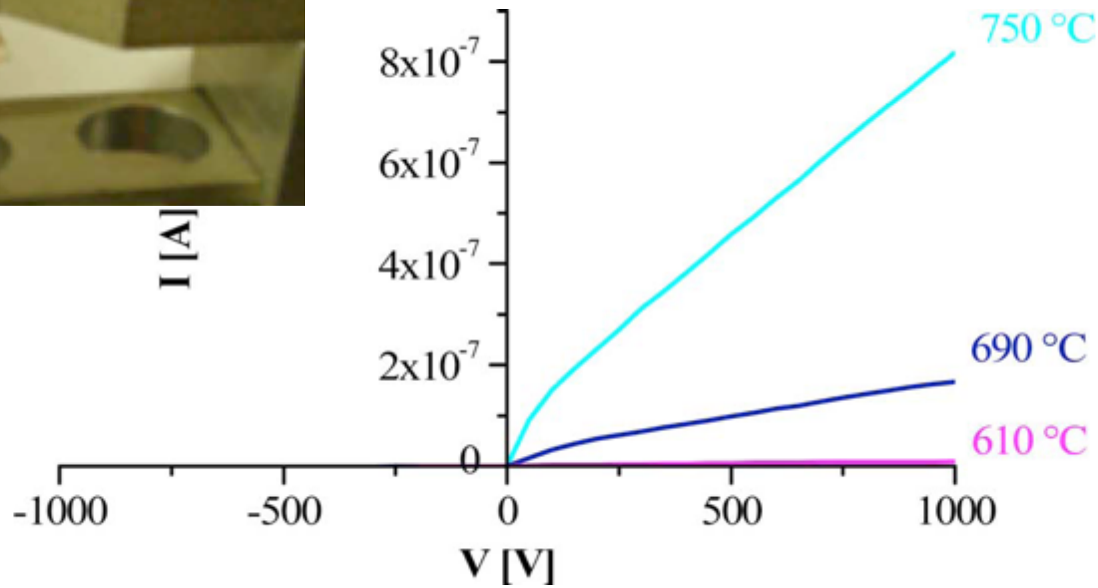
- Bias V=1000 V
- Electrode-oxide spacing d= 1mm
- Sensor T: 500-700 °C

$\}$ E =10^6 V/m



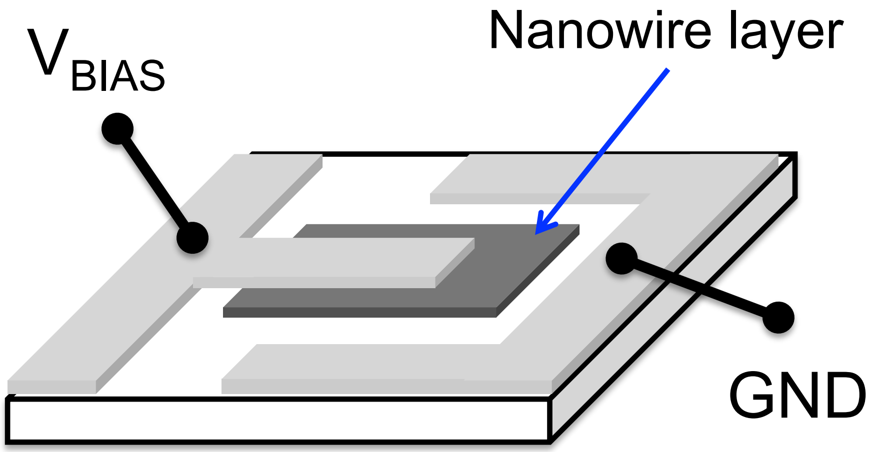
1% of ethyne in air
•positive ions generation
•Different electrode temperatures

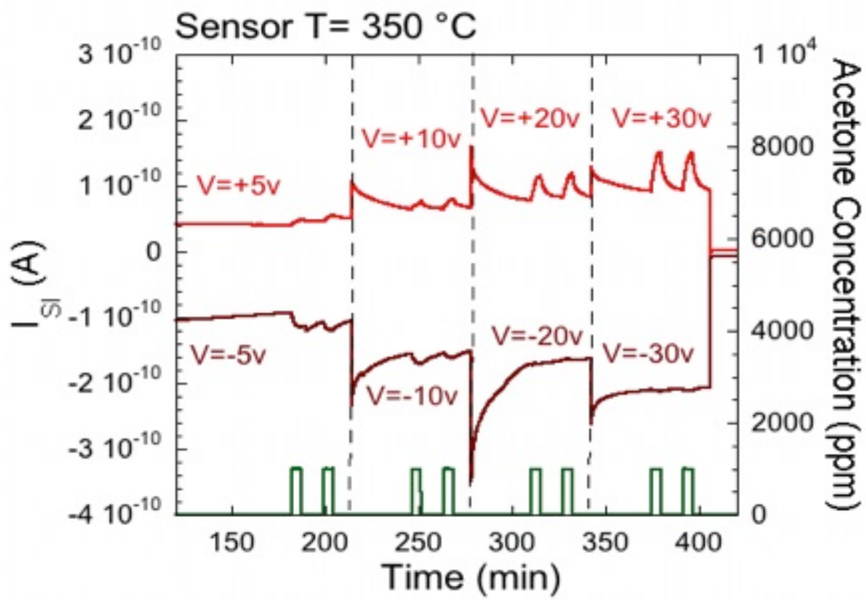
Asymmetric I-V curve

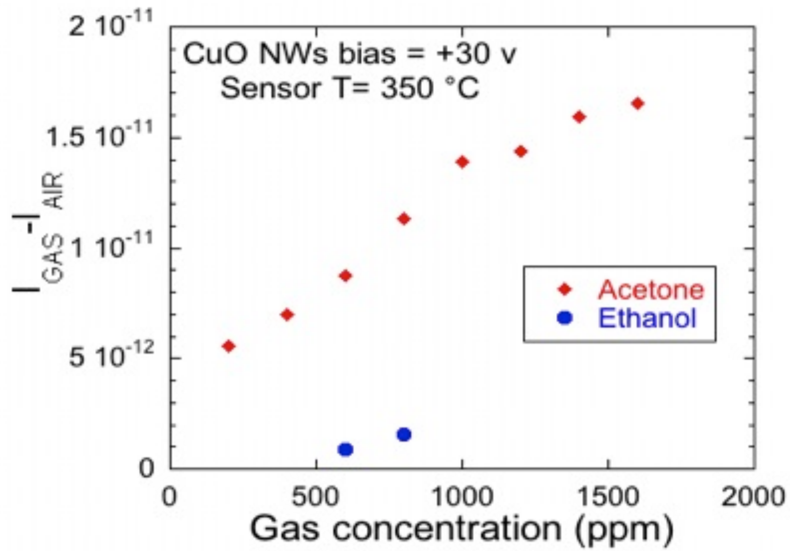


A. Hackner, A. Habauzit, G. Müller, E. Comini, G. Faglia, and G. Sberveglieri; IEEE Sens. J. 9 (2009) 1727

Surface ionization (SI) - horizontal layout







- Only CuO positively biased shows response to gases;
- Response to ethanol is much lower than the response to acetone (in agreement with first ionization energy values);
- SI response measured at much lower electric field (150 V/cm) with respect to the vertical layout

Quasi 1D in thermoelectrics

$$ZT = \frac{\alpha^2 \sigma T}{k}$$

LETTERS

Silicon nanowires as efficient thermoelectric materials

LETTERS

Enhanced thermoelectric performance of rough silicon nanowires

Allon I. Hochbaum[1*], Renkun Chen[2*], Raul Diaz Delgado[1], Wenjie Liang[1], Erik C. Garnett[1], Mark Najarian[3], Arun Majumdar[2,3,4] & Peidong Yang[1,3,4]

NANO LETTERS
pubs.acs.org/NanoLett

Reduction in the Thermal Conductivity of Single Crystalline Silicon by Phononic Crystal Patterning

Patrick E. Hopkins,† Charles M. Reinke,† Mehmet F. Su,† Roy H. Olsson III,† Eric A. Shaner,† Zayd C. Leseman,† Justin R. Serrano,† Leslie M. Phinney,† and Ihab El-Kady*,†,†

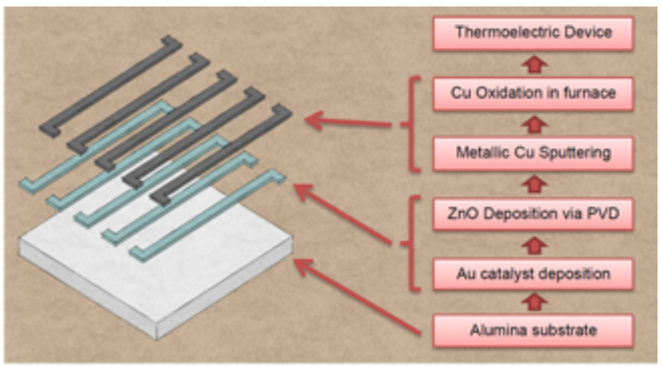
GY

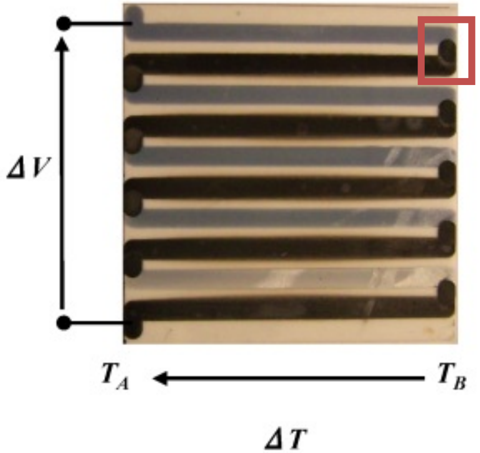
❖ Improvements due to:

- K reduces more than σ based on difference between electrons and phonons scattering length
- S is propto the energy derivative of the density of electronic states (quantum confinement)
- Excellent durability of metal oxides at high temperatures for high-temperature thermoelectric applications.
- Quasi 1D metal oxide nanowires have indeed already shown a suppressed thermal conductivity due to increase of phonon-boundary scattering, and an impressive high mobility.
- Metal oxide nanowires appears as candidates for developing high temperature efficient thermoelectric generator

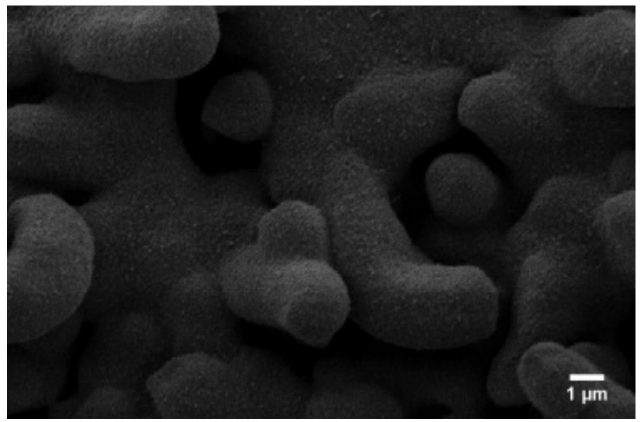
Planar thermoelectric generator (TEG) made by oxide nanowires ZnO-n/CuO-p

- ❖ Five thermocouples based on metal-oxide nanostructured elements wired electrically in series and thermally in parallel
- ❖ ZnO (*n*-type) deposited at 800degC and CuO (*p*-type) oxidized at 400degC
- ❖ Bundles of quasi-monodimensional nanowires deposited as thin layers employing shadow masks
- ❖ 20 mm x 20 mm alumina substrates
- ❖ Each element consists of an *S*-shape strip with 20 mm length and 1 mm width





a



b

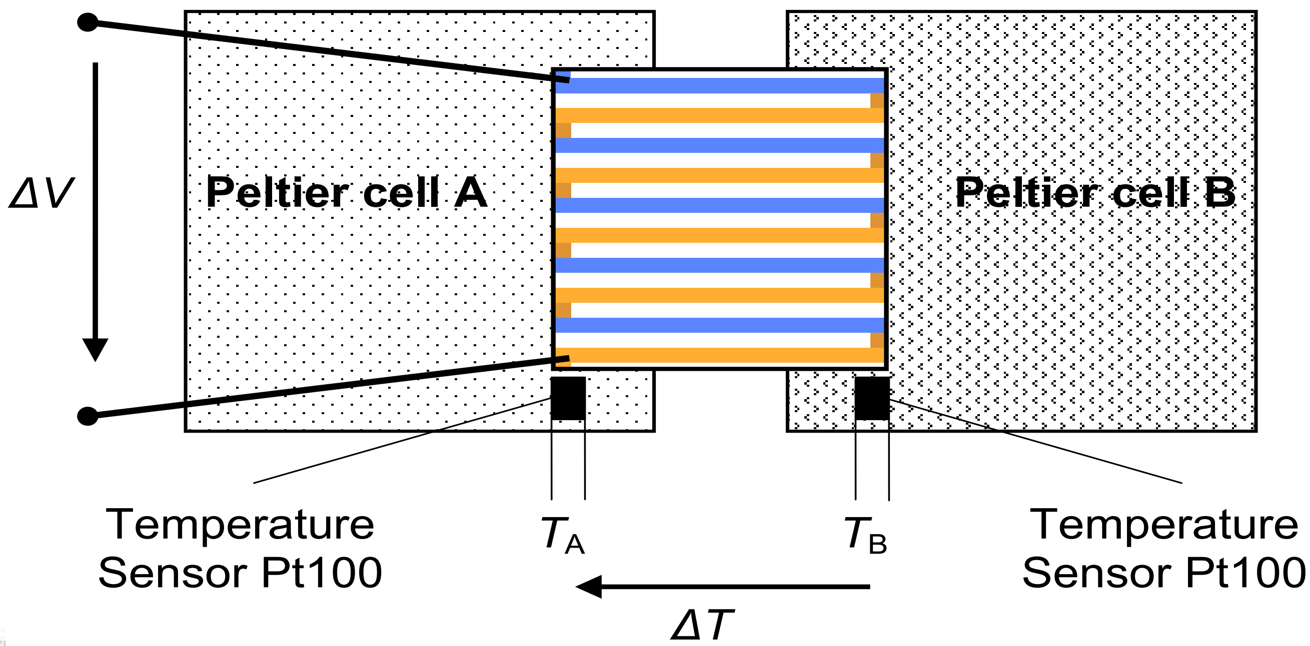
Experimental characterization: TEG

- Temperature difference $\Delta T = T_A - T_B$ applied to the sample
- Measurement of the generated voltage ΔV as a function of the applied temperature difference ΔT

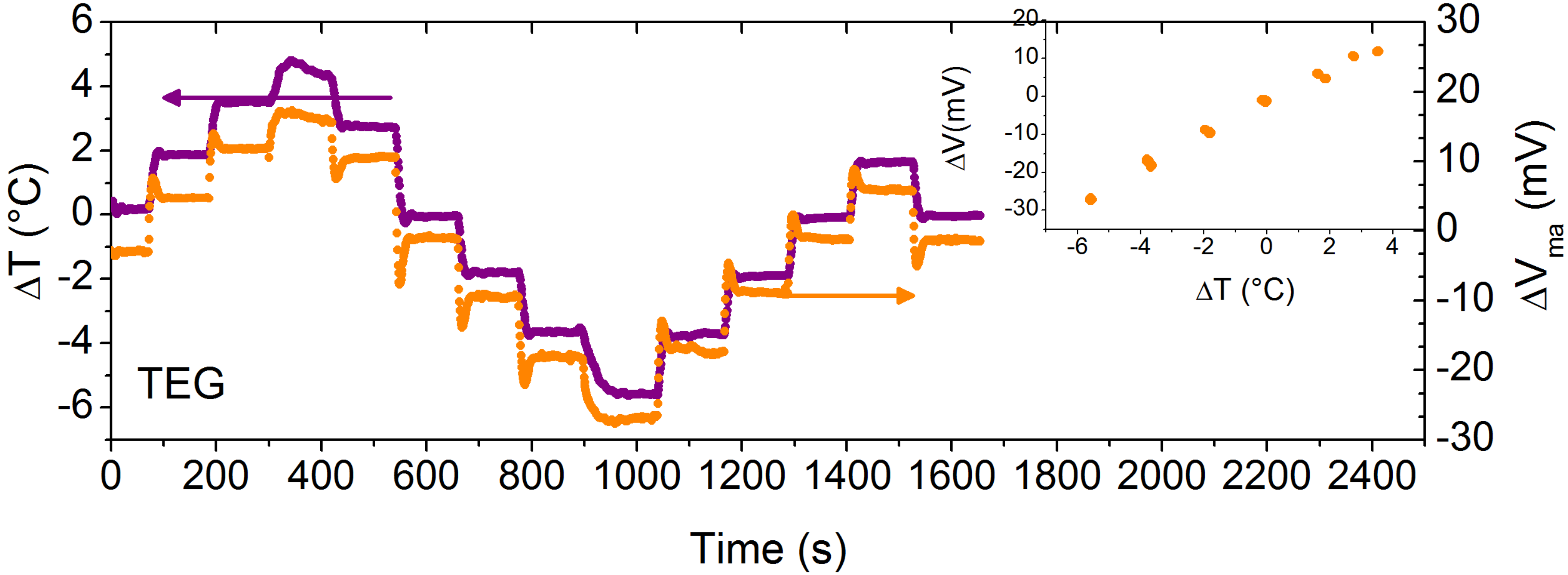
$$\Delta V = S\Delta T = N\alpha_{pn}\Delta T$$

S Seebeck coefficient of the thermoelectric generator
$N = 5$ number of thermocouples
α_{pn} Seebeck coefficient of a single ZnO-CuO thermocouple

Experimental set-up



Experimental results: TEG



S = 4 mV/°C
α_{pn} = 0.8 mV/°C
R= 9MΩ

$$PF = \frac{P_{MAX}}{\Delta T^2 A} = \frac{0.4\ pW / K^2}{A} = 1\ \mathrm{n}W / K^2 m^2$$

Results

- A planar thermoelectric generator (TEG) containing five ZnO (*n*-type) and CuO (*p*-type) thermocouples based on metal-oxide nanostructured elements wired electrically in series and thermally in parallel has been built with the future aim to powering autonomous sensor microsystems.
- Seebeck coefficient @RT of the thermoelectric generator
  S = 4 mV/K
- Seebeck coefficient of a single ZnO-CuO thermocouple
  α_{pn} = 0.8 mV/K. Resistance is still a way too high
- Feasibility of fabricating planar thermoelectric generators based on metal-oxide nanowires
- Fabrication of 4-terminals thermoelectric device and electrical characterization of individual nanowires

Conclusions

- The fundamental properties of nanosized materials have been studied over the last years with particular focus on the possibility to exploit the preparation of **new devices such as gas sensors, biosensors**
- A great effort has been done to **understand** and **control** the **growth process** for the production of high quality quasi one-dimensional nanostructures with bottom up techniques and their integration in functional devices.
- Different ways to **exploit** NWs peculiarities have been proposed to obtain chemical sensors
- There will be a bright future for the gas sensors ?

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Thank to the SENSOR Lab members!

THANK YOU FOR YOUR ATTENTION !

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❖CuO nanosphere at SENSOR Lab!!

❖http://sensor.ing.unibs.it